OF

ORGANIC CHEMISTRY.

BY

A. F. HOLLEMAN, Ph.D., F.R.A.Amst.,
Professor Ordinarius in the University of Amsterdam.

EDITED BY

A. JAMIESON WALKER, Ph.D. (Heidelberg), B.A.,
Head of the Department of Chemistry, Technical College, Derby, England.

ASSISTED BY

OWEN E. MOTT, Ph.D. (Heidelberg).

WITH THE CO-OPERATION OF THE AUTHOR.

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AUTHOR'S PREFACE TO THE THIRD EDITION.

ALTHOUGH less than three years have elapsed since the second edition of this book was published, recent advances in chemistry have necessitated a complete re-casting of several chapters. That treating of the proteïns has been re-written, and is now placed after the sugars, along with the chapter on amino-acids, so that it is no longer an appendix to the system of classification of organic compounds, but is incorporated with it. The book has also been brought up to date by numerous smaller changes and additions, and by the deletion of obsolete matter.

I am under an obligation to Dr. JAMIESON WALKER in the first place for having introduced into the book the proteïn-classification adopted by the CHEMICAL SOCIETY OF LONDON, the ENGLISH PHYSIOLOGICAL SOCIETY, the AMERICAN PHYSIOLOGICAL SOCIETY, and the AMERICAN SOCIETY OF BIOLOGICAL CHEMISTS; and further for the care he has bestowed on the revision of this new edition.

Besides the four editions of the original Dutch volume and three in English, seven editions of this book have been published in German, two in Russian, two in Italian, and one in Polish. A French edition and a Japanese edition are also in preparation.

A. F. HOLLEMAN.

AMSTERDAM, March, 1910.

AUTHOR'S PREFACE TO THE SECOND EDITION.

RECENT researches on the constitution of benzene have shown that neither the centric formula nor any of the other formulæ suggested affords a wholly satisfactory explanation of the observed facts. I have therefore thought it best to give the formulæ of KEKULÉ, VON BAEYER, and THIELE side by side, with a brief explanation of each.

Professor CIAMICIAN'S lecture before the German Chemical Society has given me the opportunity of rewriting completely the chapter on pyrrole.

The fifth edition of the German translation of this book has been published, and it has also been translated into Italian and Russian.

When this book is read for the first time, the matter printed from small type should be omitted, as it contains numerous references to subsequent portions of the text. Such references are in great measure avoided in the part printed from large type.

A. F. HOLLEMAN.

AMSTERDAM, January, 1907.

AUTHOR'S PREFACE TO THE FIRST EDITION.

Most of the short text-books of Organic Chemistry contain a great number of isolated facts; the number of compounds described in them is so considerable as to confuse the beginner. Moreover, the theoretical grounds on which this division of the science is based are often kept in the background; for example, the proofs given of the constitutional formulæ frequently leave much to be desired. However useful these books may be for reference, they are often ill-suited for text-books, as many students have learned from their own experience.

In this book I have endeavoured to keep the number of unconnected facts within as narrow limits as possible, and to give prominence to the theory underlying the subject. For this reason, a proof of the structure of most of the compounds is given. This was not possible for the higher substitution-products of the aromatic series, so that the methods of orientation employed in it are described in a special chapter.

Physico-chemical theories, such as the laws of equilibrium, ionization, and others, are becoming more and more prominent in organic chemistry. I have attempted in many instances to show how useful they are in this branch of the science. Such important technical processes as the manufacture of alcohol, cane-sugar, etc., are also included. The book is essentially a text-book, and makes no claim to be a "Beilstein" in a very compressed form.

I am deeply indebted to Dr. A. Jamieson Walker for the excellent way in which he has carried out the difficult task of translating this book from the original second Dutch edition into English. Lastly, it may be mentioned that it has also been translated into German, the second edition having just appeared, and that an Italian edition is in preparation.

A. F. Holleman.

Groningen, Netherlands, November, 1902.

EDITOR'S PREFACE TO THE THIRD EDITION.

THE manuscript for the third edition has been carefully revised, and many alterations and additions have been made. I have to thank Professor HOLLEMAN for the large amount of time and energy he has devoted to this work. The re-arrangement of the matter has made it necessary to re-number the paragraphs from § 199 onwards, a fact to be borne in mind when comparing the present issue with previous editions.

To several readers who have drawn my attention to errors in the text and to other points needing revision, and thus materially assisted me in preparing the manuscript for the press, I desire to express my sense of obligation.

A. JAMIESON WALKER.

DERBY, ENGLAND, March, 1910.

EDITOR'S PREFACE TO THE SECOND EDITION.

THE demand for the first English edition of this text-book, published four years ago, has been so great as to exceed anticipation, and it has been necessary to print a short edition from the existing plates during the revision of the text for the present issue.

The translation is based on the third Dutch edition of the author's "Leerboek der Organische Chemie," but the progress of the science has necessitated numerous and extensive alterations. I have to thank Professor HOLLEMAN for the great trouble he has taken in the selection and arrangement of the large amount of new work now included. The resetting of the whole book, from new type specially cast, has enabled me to rewrite the text completely.

I am again indebted to Dr. OWEN E. MOTT for important aid; to Professor SENIER for valuable advice and criticism; and to many others for their kind expressions of appreciation and commendation.

References in the text to "Laboratory Manual" allude to my translation of Professor HOLLEMAN'S "Laboratory Manual of Organic Chemistry for Beginners," published by Messrs. JOHN WILEY & SONS. This work constitutes an appendix to the text-book, and should be employed as a guide to laboratory work prior to that systematic course of preparations essential to progress in the study of organic chemistry.

A. JAMIESON WALKER.

DERBY, ENGLAND, January, 1907.

EDITOR'S PREFACE TO THE FIRST EDITION.

THE cordial reception met with by Professor HOLLEMAN'S "Leerboek der Organische Chemie" in Holland, as well as by Dr. HOF'S translation in Germany, makes it desirable that English-speaking students of chemistry should share in the advantages derived from its publication by their fellow-students on the Continent of Europe.

This translation is from the second Dutch edition, published last year, and has been revised and added to by Professor HOLLEMAN and myself so as to make it as up-to-date as possible. An Italian translation of this English edition is now in preparation. The "Inorganic Chemistry" referred to in the text is Dr. COOPER'S translation of Professor HOLLEMAN'S "Leerboek der Anorganische Chemie," published last April by Messrs. JOHN WILEY & SONS.

I have to express my thanks to Professor HOLLEMAN for the great care bestowed by him on the work of revision; to Dr. OWEN E. MOTT for his valuable assistance; to Professor SENIER of Queen's College, Galway, for reading the proof and making many important suggestions; to Dr. JOHN E. MACKENZIE of the Birkbeck Institution, London, for reading part of the proof; to Dr. HERMON C. COOPER of Syracuse University for the note regarding the law regulating the sale of alcohol in the United States; and to Messrs. JOHN WILEY & SONS for the excellent way in which they have prepared the book for publication.

A. JAMIESON WALKER.

DERBY, ENGLAND, December, 1902.

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ORGANIC CHEMISTRY.

INTRODUCTION.

1. Organic Chemistry is the Chemistry of the Carbon Compounds. The word "organic" has now lost its historic meaning, given it at a time—the beginning of last century—when it was thought that the substances which occur in *organized* nature, in the animal and vegetable kingdoms, could only be formed under the influence of a special, obscure force, called the *vital force.* Several unsuccessful attempts to prepare artificially such "organic" substances promoted this belief. Until about the year 1840, it was so general that BERZELIUS still thought that there was but little hope of ever discovering the cause of the difference between the behaviour of the elements in the mineral kingdom and in living bodies. Organic chemistry included the study of those compounds which occur in plants and animals, as well as of the more or less complicated decomposition-products which could be prepared from these compounds by various means. Among the latter many were known which were not found in nature, but it was thought impossible to build up a compound body from its decomposition-products, or to obtain an organic compound from its elements.

In the year 1828, WÖHLER had indeed obtained from inorganic sources the organic compound *urea*, a product of the animal economy. This discovery was at first regarded as of small importance, for it was thought that this substance occupied a position midway between organic and inorganic compounds. For a number of years the synthesis of urea was in fact the only well-known example of the kind, such observations becoming more numerous about the middle of the nineteenth century. At length the synthesis of many substances, including that of acetic acid by Kolbe and of the fats by Berthelot, strengthened the growing conviction that organic compounds are formed under the influence of the same forces as are inorganic, and that to this end no *special* force is necessary.

The natural distinction between organic and inorganic chemistry was thus destroyed, its place being taken by an artificial one. As it had been already noticed that all organic compounds contain carbon, the name "Organic Chemistry" was appropriated to the *Chemistry of the Carbon Compounds.*

Through the numerous discoveries which were made in this branch of the science, especially in Germany by Liebig, Wöhler, and their pupils, and in France by Dumas, Laurent, and Gerhardt, organic chemistry acquired by degrees a totally different aspect, and the old division into groups of substances which had either the same origin, as in the case of vegetable chemistry or animal chemistry, or had single properties in common, as, for example, the vegetable acids, the vegetable bases, and neutral vegetable bodies, vanished. Its place was taken by a more rational classification, which gradually developed into its present form, and is based on the mutual relationships found to exist between organic compounds.

2. Since no essential distinction between organic and inorganic chemistry now exists, and numerous syntheses have set at rest all doubt as to the theoretical possibility of building up from their elements even the most complicated carbon compounds, such as the proteïns, the question may arise as to the reason for still treating the chemistry of the carbon compounds as a special part of the science. The answer to this question is twofold.

First, the enormous number of carbon compounds which are known. This amounts to more than a hundred thousand,* and is greater than that of the compounds of all the other elements. Second, the special nature of certain properties of the carbon compounds. These are either not found at all in the compounds of other elements, or at most in a much less marked degree: for example, many inorganic compounds can be exposed to high temperatures without undergoing

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* In Richter's "Lexikon der Kohlenstoffverbindungen" and its three supplementary volumes, 112164 compounds are enumerated.

any chemical change, whereas the carbon compounds, almost without exception, are decomposed at a red heat. It follows that the latter are usually much less stable than the former towards chemical and physical reagents, and in consequence different methods are employed in the investigation of carbon compounds and of inorganic compounds.

Another peculiarity is that numerous organic compounds contain the same elements in the same proportions, but differ from one another in properties. For example, up to the end of the year 1902, one hundred and thirty-five compounds of the formula $C_{10}H_{13}O_2N$ had been discovered. This phenomenon is called *isomerism*, and is almost unknown in inorganic chemistry, a fact which necessitates an investigation of the cause to which it is due.

All these reasons make it desirable to treat the carbon compounds in a special part of chemistry.

QUALITATIVE AND QUANTITATIVE ANALYSIS.

3. Investigation has shown that in most of the compounds of carbon there is only a very small number of elements. The chief of these are *carbon, hydrogen, oxygen,* and *nitrogen. Halogen* derivatives are less numerous, and substances containing *sulphur* or *phosphorus* occur still less frequently. Carbon compounds are also known in which other elements are found, but they are exceedingly few in comparison with those which contain only the elements named above. Some elements do not occur in carbon compounds.

In order to be able to determine the nature of a compound, it is first of all necessary to ascertain what elements it contains by submitting it to *qualitative analysis.* In the case of the carbon compounds, this is very simple in theory, the process being one of oxidation.

On solution of an organic compound, the elements constituting it are usually not present as ions in the liquid. Oxidation, however, either converts them at once into ions, or into oxygen compounds with ionized groups, such as CO_3'', SO_4'', and so on. They can then be identified by the ordinary inorganic reactions ("Laboratory Manual," I, 1–5).

Carbon is thus converted into carbon dioxide, which can be detected by the lime-water test; sulphur and phosphorus are oxidized to sulphuric acid and phosphoric acid respectively; hydrogen is oxidized to water; and nitrogen is evolved in the free state.

If an organic compound contains a halogen, it is oxidized in presence of silver nitrate, the corresponding silver halide being formed. Other elements present are found, after oxidation, in the form of compounds easily identified.

For analytical purposes, oxidation is carried out in different ways, according to the nature of the element suspected to be present. Copper oxide is generally used in testing for carbon, hydrogen, and nitrogen. The substance is mixed with it, and the mixture heated in a glass tube sealed at one end, the carbon and hydrogen being oxidized by the action of the oxygen of the copper oxide. Nitrogen is evolved in the free state, and can be recognized in exactly the same way as in the quantitative analysis of nitrogen (7). For the halogens, sulphur, phosphorus, etc., it is best to oxidize the substance under examination with concentrated nitric acid.

The method of oxidation is a general one for qualitative analysis: it can always be applied, and yields positive results. There are other methods which in many cases attain the desired end more quickly and easily, but as most of these are not of universal application, the failure of one of them to detect an element affords no certain indication of its absence. In doubtful instances the question must be decided by the oxidation-process.

For example, the presence of carbon can frequently be detected by submitting the substance to dry distillation. Charring often takes place, or vapours are evolved which can be recognized as carbon compounds by their smell or other properties, such as their burning with a smoky flame on ignition.

4. The nitrogen in many organic compounds can be converted into ammonia by heating them with soda-lime, or with concentrated sulphuric acid. Another method very largely used in testing for this element was suggested by LASSAIGNE. It consists in heating the substance under examination with a small piece of sodium (or potassium) in a narrow tube sealed at one end. Should the compound contain nitrogen, sodium (or potassium) cyanide is formed, its presence being readily recognized by converting it into Prussian blue ("Laboratory Manual," I, 3, *a*).

5. The halogens can be recognized by heating the substance with quicklime, the corresponding calcium halide being formed. A very delicate method of detecting them is to introduce a small quantity of the compound on a piece of copper oxide into a non-luminous flame. The corresponding copper halide is formed and volatilizes, imparting a magnificent green colour to the flame. These two methods are always applicable.

Sulphur can often be detected by heating the compound with a small piece of sodium in a narrow ignition-tube. Sodium sulphide is produced, and can be detected by treating the reaction-mixture, placed on a clean silver coin, with water, when a black stain of silver sulphide is formed. Or, the reaction-mixture can be extracted with water, and sodium nitroprusside added: the solution acquires an intense violet colour.

No qualitative reaction is known for detecting oxygen in an organic compound. This can only be effected by a quantitative analysis.

6. Following on qualitative, must come *quantitative, analysis;* that is, the determination of the quantity of each element present in the compound. The methods used for qualitative analysis in inorganic chemistry are often very different from those employed in quantitative determinations: in organic chemistry the methods of qualitative and quantitative analysis are alike in principle, oxidation being employed in both.

Carbon and hydrogen are always estimated together. The principle of the method of organic analysis chiefly used was worked out by Liebig (1803–1873). It is usually carried out as follows. In the combustion-furnace, *k* (Fig. 1), is a hard glass tube, *ab*, open at both ends. A complete drawing of it is shown in the figure above the furnace. It contains granulated copper oxide,

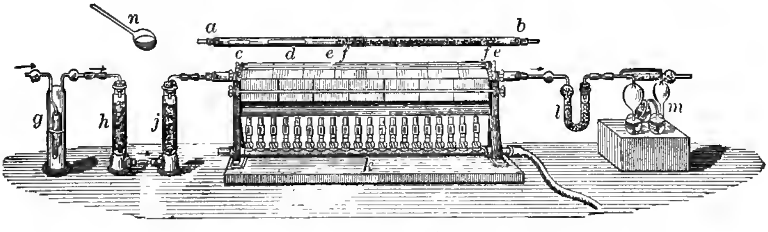


Fig. 1.—Organic Analysis.

ff, and a spiral of copper-gauze, *c*, oxidized by heating to redness in the air or in a stream of oxygen. About one-third of the length of the tube is left empty, and into this, after temporary removal of the copper spiral, a platinum or porcelain boat, *d*, containing a weighed quantity of the substance to be analyzed, is introduced. The end of the tube next the boat is connected with a drying apparatus, *g*, *h*, *j*, in which the air or oxygen is freed from water-vapour and carbon dioxide: *g* contains concentrated caustic potash, *h* soda-lime, and *j* calcium chloride. To the end of the tube furthest from the boat is attached a weighed calcium-chloride tube, *l*, for the purpose of collecting the water produced by the combustion of the substance. The weighed potash-bulbs, *m* (shown enlarged in Fig. 2), are connected to this, and in them the carbon dioxide formed is absorbed by concentrated caustic potash. The gases enter the apparatus by the tube *b* on the right, pass through the three bulbs containing potash, and escape through the tube *a*, which is filled with soda-lime. As soon as all the joints of the apparatus are known to be gas-tight, the burners are lighted, except beneath the place where the boat is. When the tube is hot, the substance is burned by carefully heating this part of the tube, while at first a slow stream of air, and later a slow stream of oxygen, is led through the drying apparatus into the tube. The oxygen facilitates the combustion of the particles of carbon which have deposited, and the red-hot copper oxide serves to oxidize the gaseous decomposition-products completely to carbon dioxide and water. The increase in weight of the calcium-chloride tube and that of the potash-bulbs respectively give the quantity of water and carbon dioxide formed, from which the amount of hydrogen and carbon in the compound can be calculated.

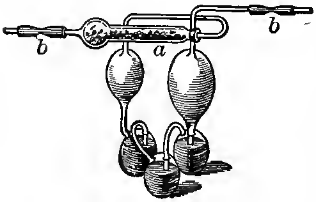


FIG. 2.—POTASH-BULBS.

If the compound contains nitrogen or halogens, a freshly-reduced spiral of copper-gauze is placed at the end of the tube next the absorption-apparatus *l* and *m*. The hot copper decomposes any nitrogen oxides formed, which would otherwise be absorbed in the potash-bulbs: it also combines with and retains the halogens.

The foregoing is only intended to illustrate the principles on which the methods of organic analysis are based. The experimental details have often to be modified somewhat to suit special circumstances. For example, substances which burn with great difficulty are mixed with lead chromate instead of copper oxide, the former being the more energetic oxidizing agent. When the compound contains sulphur, this substance is also used, the sulphur being converted, by heating in contact with the chromate, into lead sulphate, which is stable at red heat. If copper oxide is used, sulphur dioxide is formed and is absorbed in the potash-bulbs, thereby introducing an error into the carbon estimation. Another method of retaining sulphur dioxide consists in having a layer of lead dioxide, PbO_2, at the end of the tube next to the absorption-apparatus. This layer is gently heated, and retains all the sulphur dioxide in the form of lead sulphate. Combustion tubes of silica are also employed, and are superior to glass in their power of resisting fracture. Contact of the copper oxide with the inner surface of the tube should be prevented by means of a layer of asbestos, to obviate the formation of copper silicate.

7. Nitrogen is usually estimated by Dumas's method. An apparatus similar to that employed in the estimation of carbon and hydrogen (Fig. 1) is used. The drying apparatus *g*, *h*, *j*, is replaced by a carbon-dioxide Kipp generator, to effect complete expulsion of the air from the tube before the combustion is begun. The absorption-apparatus *l*, *m*, is replaced by a delivery-tube opening under mercury. As soon as the air has been driven out of the apparatus, the front part of the tube, containing the copper-gauze and the granulated copper oxide, is heated. The combustion is then begun, and the evolved gases are collected in a graduated tube open at the bottom (measuring tube), the end of which dips into the mercury-bath. This tube is filled partly with mercury, and partly with concentrated caustic potash to absorb the carbon dioxide. The reduced copper-gauze has the effect of decomposing any nitrogen oxides formed. When the combustion is over, all the nitrogen remaining in the tube is swept into the graduated tube by a stream of carbon dioxide from the Kipp generator. The tube, along with the mercury, potash, and gas which it contains, is then placed in a wide cylinder filled with water. The mercury and potash are displaced by the water, and

after the level of the liquid inside and outside the tube has been made to coincide, the number of cubic centimetres of nitrogen is read off. From this the amount of nitrogen in the compound is calculated.

Nitrogen can often be estimated by a method discovered by KJELDAHL and improved by WILFARTH. It depends upon the fact that the nitrogen of many organic substances is wholly converted into ammonia by heating the compound for some time with concentrated sulphuric acid in presence of phosphoric oxide and a drop of mercury, the latter going into solution. Usually the mixture first turns black, owing to charring: after heating for one or two hours the liquid again becomes perfectly colourless. The carbon has then been fully oxidized by the oxygen of the sulphuric acid, which has been reduced to sulphurous acid. The process is facilitated by the mercury salt, which probably plays the part of an "oxygen-carrier" between the sulphuric acid and the organic substance, being continually converted from the mercuric to the mercurous state, and then back again by the boiling acid into the mercuric state. When the liquid has become colourless, it is allowed to cool, diluted with water, excess of alkali added, and the ammonia distilled into a measured quantity of acid of known strength. Titration gives the quantity of ammonia, and hence the amount of nitrogen. This neat and simple method is usually not applicable to compounds containing oxygen linked to nitrogen. In such compounds the nitrogen is only partially converted into ammonia.

8. The halogens can be estimated by the method either of LIEBIG or of CARIUS. By the former, the substance is heated with quicklime, and by the latter, at a high temperature with a small quantity of concentrated nitric acid and a crystal of silver nitrate in a sealed glass tube. This is carried out without risk in the tube-furnace (Fig. 3), in which the glass tubes are placed in wrought-iron cylinders with thick walls.

CARIUS's method can also be applied to the estimation of sulphur, phosphorus, and other elements. Non-volatile substances containing sulphur or phosphorus can also be oxidized by fusion with nitre.

The estimation of halogens in solids can also be readily effected by oxidation with sodium peroxide, the final product being a chlorate, bromate, or iodate. On reduction with sulphurous acid, this is converted into a halide, which can be precipitated with silver nitrate in the usual manner.

9. The results of a quantitative analysis are expressed in percentage-numbers. If the total of these percentage-numbers is very nearly 100, then no other element is present in the compound; but if appreciably less than 100, there is another element present which has not been taken account of in the analysis, there being no convenient method for its estimation. This element is *oxygen*. The percentage-amount of oxygen is therefore found by subtracting the total of the percentages of the other elements from 100. This has the disadvantage that all experimental errors are included in the percentage-number of the oxygen.

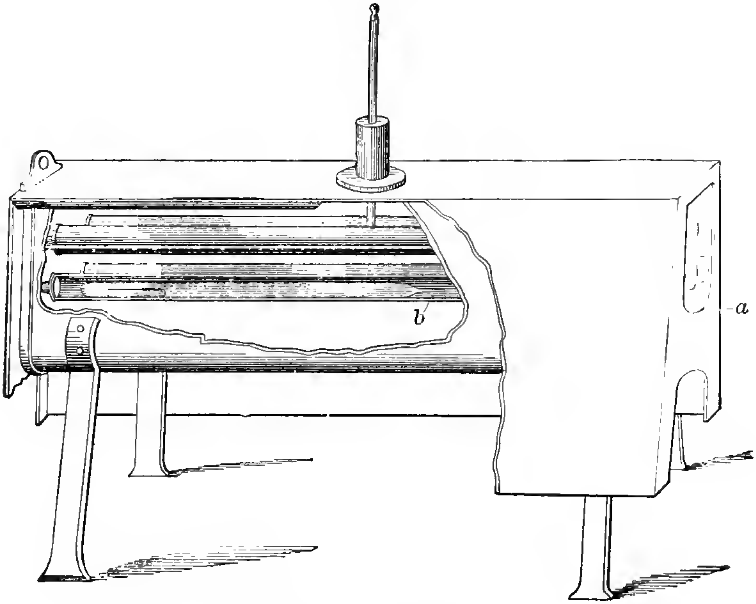


Fig. 3.—Tube-furnace.

Carbon-estimations are usually too low, owing to the loss of a small quantity of carbon dioxide through the various connections of the apparatus. Hydrogen-estimations are generally too high, because copper oxide is hygroscopic, and can only be freed from traces of moisture with difficulty. These errors balance one another more or less, so that the want of accuracy in the oxygen-percentage is diminished.

The method by which the percentage composition and formula of a substance are calculated from the results of analysis is best explained by an example.

The analysis of a substance containing nitrogen yielded the following numbers:

0·2169 g. substance gave 0·5170 g. CO_2 and 0·0685 g. H_2O.

0·2218 g. substance gave 17·4 c.c. N, measured over water at 6° C. and 762 mm. barometric pressure.

Since there are 12 parts by weight of C in 44 parts by weight of CO_2, and 2 parts by weight of H in 18 parts by weight of H_2O, the number obtained for CO_2 must be multiplied by $\frac{12}{44}=\frac{3}{11}$ to find the weight of C, and the number found for H_2O by $\frac{2}{18}=\frac{1}{9}$ to obtain the weight of H. This calculation gives 65·0 per cent. of carbon and 3·51 per cent. of hydrogen in the compound.

The weight of the nitrogen is calculated as follows. Since it is saturated with water-vapour, the tension of this expressed in mm. of mercury must be subtracted from the barometric pressure in order to obtain the true pressure of the nitrogen. At 6° C. the tension of aqueous vapour is 7·0 mm. The actual pressure of the nitrogen is therefore $762-7=755$ mm. Since 1 c.c. of nitrogen at 0° and 760 mm. weighs 1·2562 mg., at 755 mm. and 6° C. the weight of this volume expressed in milligrammes is

$$\frac{1\cdot2562}{1+6\times0\cdot00367}\times\frac{755}{760}=1\cdot2211.$$

Therefore the 17·4 c.c. of nitrogen obtained weigh $1\cdot2211\times17\cdot4=21\cdot247$ mg., from which the percentage of nitrogen is found to be 9·6.

The sum of these percentage-numbers is 78·1, so that the percentage of oxygen in the substance analyzed is 21·9. The percentage-composition given by the analysis is therefore

C	65·0
H	3·5
N	9·6
O	21·9

On dividing these values by the numbers representing the atomic weights of the corresponding elements, there results

C	H	N	O
5·4	3·5	0·7	1·4.

These numbers divided by 0·7 give

C	H	N	O
7·7	5·0	1·0	2·0.

These numbers approximate very closely to those required by the formula $C_8H_5O_2N$. The percentage-composition corresponding to this formula is

C 65·3 H 3·4 N 9·5,

which agrees well with the analysis.

DETERMINATION OF MOLECULAR WEIGHT.

10. An analysis only gives the empirical formula of a compound, and not its molecular formula, because $C_aH_bO_c$ has the same percentage-composition as $(C_aH_bO_c)_n$. When the empirical formula has been ascertained by analysis, the *molecular weight* has still to be determined.

It cannot be decided by chemical means, although it is possible thus to obtain a minimum value for the molecular weight. For example, the empirical formula of benzene is CH. Benzene readily yields a compound, C_6H_5Br, which can be reduced again to benzene. It follows that the molecule of benzene must be represented by C_6H_6 at least. The molecular formula, however, could also be $C_{12}H_{12}$, or, in general, $(C_6H_6)_n$; the bromine compound would then have the formula $(C_6H_5Br)_n$. Assuming the formula to be $C_{12}H_{12}$, that of the bromine compound would be $C_{12}H_{10}Br_2$. It is evident that the formation of a compound of this formula would involve direct replacement of two hydrogen atoms by bromine, and experiments would be made for the purpose of obtaining $C_{12}H_{11}Br$. Should these not attain the desired result, the probability of the correctness of the simpler formula C_6H_5Br would be increased. This would not, however, be decisive, because the experimental conditions necessary to the formation of the compound $C_{12}H_{11}Br$ might not have been attained. The chemical method only proves that the molecular formula of benzene cannot be smaller than C_6H_6, but does not prove whether it is a multiple of this or not.

To ascertain the real molecular weight, physical methods must be employed. These involve the determination either of the specific gravity of the compound in the gaseous state, or of certain values depending on the osmotic pressure of the substance in dilute solution. The theory of these methods is fully explained in "Inorganic Chemistry," 31–34 and 40–43. Here it will suffice to describe the practical details of a molecular-weight determination.

In calculating the *vapour-density* (the specific gravity of the substance in the gaseous state), four quantities—the weight of substance converted into the gaseous state, the volume of the resulting vapour, the temperature at which the volume is measured, and the barometric pressure—must be known.

11. Vapour-density is usually determined by a method suggested by VICTOR MEYER. The apparatus (Fig. 4) consists of a glass tube *B* with an internal diameter of about 4 mm. This tube is closed at the top with a stopper, and underneath has a wider cylindrical portion of about 200 c.c. capacity, closed at the lower end. Near the top of the tube is sealed on a delivery-tube *A* for the gas, which is collected over water in a graduated tube *E*. The apparatus is partly surrounded by a wide glass (or metal) jacket *C*. This contains a liquid boiling higher than the substance the vapour-density of which is being determined. This liquid is heated to boiling, some of the air in *B* being in consequence expelled. A point is soon reached at which no more air escapes from the delivery-tube, that in the wider part of the tube having a constant temperature, almost equal to that of the vapour of the boiling liquid. The graduated tube is then filled with water and placed over the open end of the delivery-tube *A*. After the stopper has been withdrawn, a weighed quantity of the substance under examination enclosed in a small glass tube is dropped into the apparatus, and the stopper replaced, care

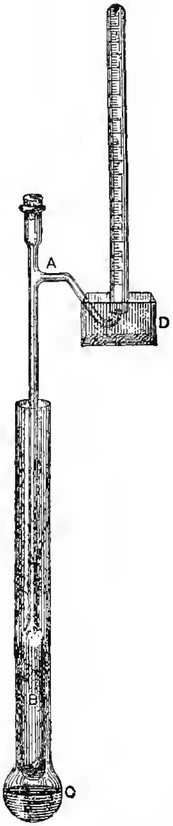


FIG. 4.—VICTOR MEYER'S VAPOUR-DENSITY APPARATUS.

being taken to make it air-tight. The substance vaporizes quickly in the heated wide portion of the tube. Its vapour expels air from the apparatus: the air is collected in the graduated tube, and its volume is equal to that of the vapour. While, however, the air in the hot part of the apparatus has the local temperature, in the graduated tube it acquires the temperature of the latter, and this must be considered in making the calculation. The experiment gives a volume equal to that which the weighed portion of the substance in the form of vapour would occupy, if it were possible to convert it into a gas at the ordinary temperature and under the barometric pressure.

For ease of manipulation this method leaves nothing to be desired. It possesses, moreover, the great advantage over the other methods, that it is not necessary to know the temperature to which the apparatus has been heated, this not being employed in the calculation. It is only necessary that the temperature should remain constant during the short time occupied by the experiment.

The result is calculated thus. Suppose that g mg. of the substance were weighed out, and yielded V c.c. of air, measured over water, with the level the same inside and outside the tube: suppose further that the barometric pressure were H, the temperature t, and the tension of aqueous vapour b, then, at a pressure of $H-b$ mm. and at $t°$, g mg. of the substance would occupy a volume of V c.c., so that under these conditions the unit of volume (1 c.c.) would contain $\frac{g}{V}$ mg. of the substance.

One c.c. of hydrogen at $H-b$ mm. of pressure, and at $t°$, weighs in milligrammes

$$\frac{0{\cdot}0895}{1+0{\cdot}00367t}\times\frac{H-b}{760},$$

from which it follows that the vapour-density D referred to hydrogen is

$$D=\frac{g}{V}\times\frac{1+0{\cdot}00367t}{0{\cdot}0895}\times\frac{760}{H-b}.$$

The molecular weight M being twice the density,

$$M=2D.$$

12. Two other methods are often employed in the determination of the molecular weights of organic compounds. They are based on the laws of osmotic pressure, and involve the determination of the depression of the freezing-point or the elevation of the boiling-point of a dilute solution of the substance, referred to the freezing-point or boiling-point respectively of the pure solvent ("Inorganic Chemistry," 40-43).

In practice, it is necessary to determine first the freezing-point of the solvent; for example, that of phenol. Then one gramme-molecule of a substance of known molecular weight is dissolved in a known weight—that is, in a known volume—of the solvent. It lowers the freezing-point by a certain amount, which is always the same for the same solvent, no matter what the substance may be, provided that the volume of solution, containing one gramme-molecule, is the same. The depression of the freezing-point caused by a gramme-molecule is, therefore, a constant for this solvent. If a one per cent. solution of a substance of unknown molecular weight M be made in phenol, and the depression (A) of the freezing-point of this determined, then

$$AM = \text{Constant};$$

because the depression of the freezing-point is, between certain limits, proportional to the concentration.

It is evident that this formula is equally applicable to the elevation of the boiling-point. Here M is the only unknown quantity, and can be calculated from this equation.

The product AM is called the *molecular depression of the freezing-point* or the *molecular elevation of the boiling-point* of the solvent.

Example.—Numerous determinations have proved that when phenol is used as the solvent the molecular depression of its freezing-point is equal to 75. We have then for phenol

$$AM = 75.$$

A solution of 2·75 per cent. concentration was prepared by dissolving 0·3943 g. of a substance of empirical formula $C_7H_7ON_2$ in 14·34 g. of phenol. The depression of this solution was 0·712°. For a one per cent. solution the depression would have been $\frac{0{\cdot}712}{2{\cdot}75} =$

0·258, therefore $A = 0{\cdot}258$. It follows that the molecular weight is $\frac{75}{0{\cdot}258} = 291$.

Since $C_7H_7ON_2$ corresponds with the molecular weight 135, and $C_{14}H_{14}O_2N_4$ to 270, the latter comes nearest to the molecular weight found, so that twice the empirical formula must be assigned to the compound.

The laws of osmotic pressure only hold when the solutions are very dilute. This is also true of the equation $AM = \text{Const.}$, since it is derived from these laws.

It is not strictly correct to determine A by means of a solution of finite concentration, as is done in the example given.

To determine M accurately, the value of A should be derived from a solution of infinite dilution; but as this is not possible, Eykman has described the following *graphic method* of determining A for such a solution. A is determined for three or four concentrations, and the values obtained are represented graphically as in Fig. 5, in which the values of A are the ordinates, and those of the percentage-strengths of the solutions are the abscissæ. Eykman states that very often the line drawn through the tops of the ordinates is very nearly straight. If it is produced till it cuts the ordinate OA, OP_0 gives the value of A for infinite dilution.

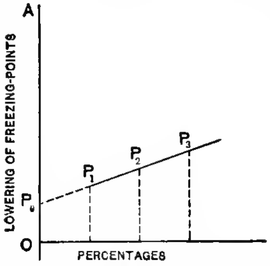


Fig. 5.—Eykman's Graphic Method.

13. The constants for the *molecular depression of the freezing-point* of a number of solvents are given in the following table:

Solvent.	Melting-point.	Molecular Depression.	
		Observed.	Calculated.
Water	0°	19	18·9
Acetic acid	16·5°	39	38·8
Benzene	6°	53	53
Nitrobenzene	5°	70	69·5
Phenol	39·6°	75	77
Naphthalene	80°	69	69·4
Urethane	48·7°	51·4	—
Stearic acid	53°	45	—
p-Toluidine	42·5°	52·4	—

The last five solvents are very useful, and are better than glacial acetic acid, which is still often employed, because they are not hygroscopic. Moreover, they melt above the ordinary temperature, so that a cooling agent is unnecessary, and their constants are high.

The following table shows that the *molecular elevations of the boiling-point* are usually smaller than the molecular depressions of the freezing-point.

Solvent.	Boiling-point.	Molecular Elevation.	
		Observed.	Calculated.
Water	100°	5·1	5·2
Ether	35·6°	22·1	21·1
Ethyl alcohol	78·0°	11·3	11·5
Benzene	80·4°	26·0	26·7
Chloroform	61·0°	35·6	36·6
Acetone	56·3°	17·3	16·7

The numbers in the last column of the tables are calculated from VAN'T HOFF's formula

$$K = \frac{0\cdot02 \times T^2}{W},$$

K being the molecular depression or elevation, T the freezing-point or boiling-point on the absolute scale, and W the latent heat of fusion or of evaporation per kilogramme of the solvent.

14. EYKMAN has constructed convenient apparatuses for the determination of the depression of the freezing-point and the elevation of the boiling-point. The first (Fig. 6) comprises a small thermometer divided into twentieths of a degree with a small flask attached as shown in the figure, this being contained in a glass cylinder: it is held at the top by a stopper, and supported underneath by cotton-wool. The latter has the effect of making

the cooling take place slowly. Being a poor conductor of heat, the cotton-wool retards cooling. A weighed quantity of the solvent is placed in the flask, and its freezing-point determined. Then a known weight of the substance is introduced, and the freezing-point again observed. From the depression of the freezing-point thus obtained *A* can be calculated as in the example given (**12**).

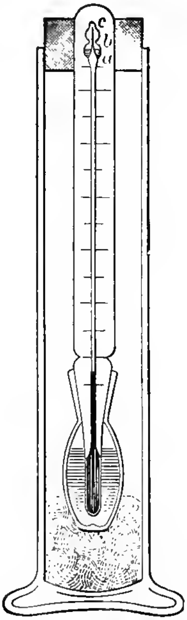


Fig. 6.—Eykman's Depressimeter.

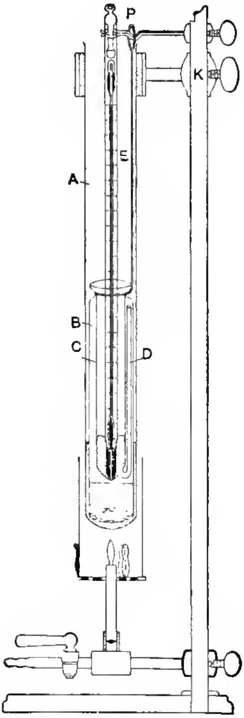


Fig. 7.—Eykman's Boiling-point Apparatus.

15. Eykman's apparatus (Fig. 7) for determining the elevation of the boiling-point comprises a thermometer, and two glass vessels, *A* and *B*. The tube *A* is about 40 cm. long and 4 cm. wide, and serves both as a heating jacket for the pure solvent, and as an air-condenser. Into *B*, which is only a few millimetres narrower than *A*, there is fused the boiling-tube *C*, with a narrow side-tube *D*. *C* is suspended from the clamp *K* by a platinum wire, *P*, twisted round its neck, and can be raised or lowered at will. The thermometer-scale is divided into tenths of a degree, the graduations being about one millimetre apart, so that with the aid of a lens it is possible to read to one-hundredth of a degree. Besides giving the boiling-point, the graduated scale of the thermometer also serves to indicate the volume of solution contained in *C*. For this purpose the vessel *C* with the thermometer placed in it must be calibrated by a gravimetric or volumetric method.

When using the apparatus the solvent is introduced into *C* until the level of the liquid has risen to that of the first graduation on the thermometer-scale, from 5 to 10 c.c. being needed. About 40 or 50 c.c. of the solvent are poured into the jacket *A*, and the apparatus heated with a micro-burner, using a large flame at first. When ebullition has begun, the size of the flame is reduced so that the vapour is completely condensed in the tube *A* at a height shown in the figure by the letters *A* or *E*.

When the liquid has boiled at a constant temperature for a short time, the height of the mercury is noted, and the clamp raised so that the open end of the boiling-tube *C* is some centimetres above the top of the jacket *A*. A weighed quantity—1–2 milligramme-molecules—of the substance under investigation is then introduced into *C* from a tared weighing-tube, and *C* gently lowered to its former position in the jacket. While the weighing-tube is being weighed to ascertain how much substance has been added, the boiling-point of the solvent will have become constant. This is noted, the boiling-tube *C* again raised by the aid of the clamp *K*, and the volume accurately determined by reading with a lens the height of the solution-meniscus on the thermometer-scale.

A second determination is made with a solution of greater concentration by introducing a further quantity of the substance from the weighing-tube, and repeating the series of operations just described. Since very little more time is needed for each operation than is required to tare the weighing-tube and its contents, a series of determinations at different concentrations can be quickly made, and the results plotted on squared paper. From the curve thus obtained the value of *A* for infinite dilution can be readily calculated (12).

THE ELEMENT CARBON.

16. Carbon occurs in three allotropic forms: *diamond*, *graphite*, and *amorphous carbon*. For a description of these the reader is referred to "Inorganic Chemistry," **176–179**, which also treats of the compounds of carbon with metalloids and metals, as well as with the determination of its atomic and molecular weights. The evidence in favour of the assumption that the molecule of carbon contains a great number of atoms is there set forth.

Confirmation of this view is afforded by a consideration of the relation subsisting between the boiling-points of the compounds of carbon and of hydrogen. If these be denoted by the general formula C_nH_{2n-p}, then, even when n and p are both large numbers, the boiling-points of these substances are relatively low, and rise with the increase of both n and p. For carbon itself, $2n = p$, and, on account of the extraordinary non-volatility of this substance, the value of n must be very great.

In direct opposition to these arguments for the assumption of a high molecular weight for carbon is the considerable depression produced in the freezing-point of iron by addition of a small proportion of carbon. Pure iron melts at about 1600°, but addition of 4·3 per cent. of carbon lowers the melting-point to 1130°. The molecular depression of iron is not large, as is proved by comparing the melting-points of iron-alloys containing a small percentage of aluminium or nickel with the melting-point of pure iron. In the equation

$$AM = \text{Constant}$$

the constant has thus a relatively small value. Therefore, the value of A being great, M, the molecular weight of carbon, must be small.

It is evident that the determination of the value of the molecular weight of carbon is a problem still awaiting solution.

VALENCY.

17. The subject of valency is treated of in "Inorganic Chemistry," **76**. With univalent elements carbon forms compounds of the type CX_4. *It is therefore quadrivalent, and it is on this foundation that the whole superstructure of organic chemistry rests.*

The compound CO_2 is also an instance of the quadrivalency of carbon. In carbon monoxide, CO, on the other hand, the carbon atom must be looked upon as bivalent, at least if the bivalency of oxygen is retained. Other compounds are well known in which carbon may be looked upon as bivalent, but their number is very small in comparison with those, numbering many thousands, in which carbon must be regarded as quadrivalent.

LABORATORY-METHODS.

18. To prevent repetition, it is desirable, before proceeding with the description of organic compounds, to give a short account of the most important operations used in their preparation and investigation.

Heating Substances Together.—This process is very often used to induce reaction between bodies, since the velocity of reactions increases largely with rise of temperature ("Inorganic Chemistry," **13** and **104**). Details vary according to the temperature to be attained. If this is considerably below the boiling-point of the most volatile compound, they are simply mixed together in a flask fitted with a thermometer, as in Fig. 8. The flask is immersed in an air-bath formed of a vertical iron cylinder closed at the lower end, a piece of stove-pipe being very suitable. The upper end is closed with a sheet of asbestos mill-board, with an opening for the neck of the flask. Should, however, the boiling-point of one of the substances be reached or overstepped, the flask must be connected with a condenser, as in Fig. 9. The invention of this form of condensing apparatus is usually attributed to Liebig, although it was first constructed by Weigel in 1771. It consists of a glass tube *aa*, enclosed in a jacket *b* of glass or metal, through which a stream of cold water can pass. For substances of high boiling-point a plain vertical glass tube may

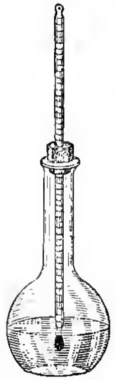


Fig. 8.—Heating Substances in an Open Flask.

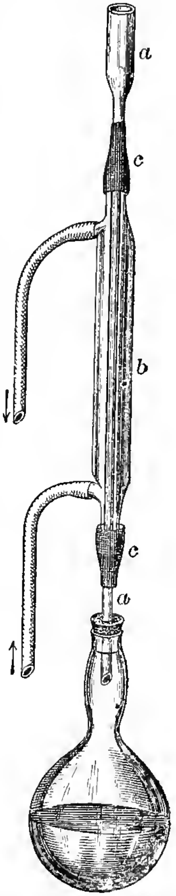


Fig. 9.—Flask with Reflux-condenser.

be substituted: it is called an "air-condenser," being sufficiently cooled by the air alone. The effect of the condenser is evident: the boiling liquid is condensed in it and drops back into the flask.

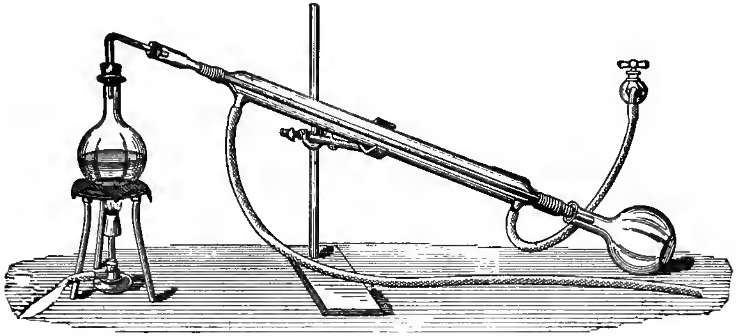


Fig. 10.—Distillation-apparatus.

When substances have to be heated above their boiling-points, they are placed in a thick-walled glass tube sealed at one end: this is then sealed at the other, and heated in a tube-furnace (9, Fig. 3).

19. *Distillation.*—The apparatus shown in Fig. 10 may be used, but if the liquid to be distilled is of such a nature that it would become contaminated by the action of its vapour on the cork or rubber stopper shown in the figure, a distilling-flask (Fig. 11) is substituted, and, if its neck is sufficiently long, contact of the vapour with the stopper during distillation is prevented.

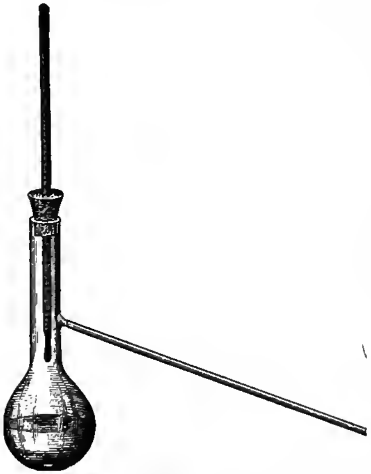


Fig. 11.—Fractionating-flask.

20. At the ordinary pressure many substances decompose on heating to their boiling-points, but distil unchanged under diminished pressure, because the boiling-point is then much lower. The apparatus shown in Fig. 12 can be used for vacuum-distillation.

The liquid to be distilled is placed in *d*. A glass tube *e*, drawn out to a very fine point, dips into the liquid, and a thermometer is placed in it. As soon as the apparatus has been made vacuous by the water-pump *w*, a stream of small bubbles of air escapes from the fine point of the tube *e*, and serves to prevent the violent "bumping" which otherwise occurs when liquids are boiled under diminished pressure. This bumping, caused by the sudden and intermittent formation of vapour, sometimes causes boiling over, or fracture of the flask. The receiver *b* is kept cool by a stream of water from *c*. *m* is a mercury manometer: *a* is a two-way stop-cock which permits access of air to the apparatus after the distillation, and also serves to cut off the connection between the air-pump and the rest of the apparatus when the pump "strikes back"; that is, when the water rises through the tube *s* into the apparatus.

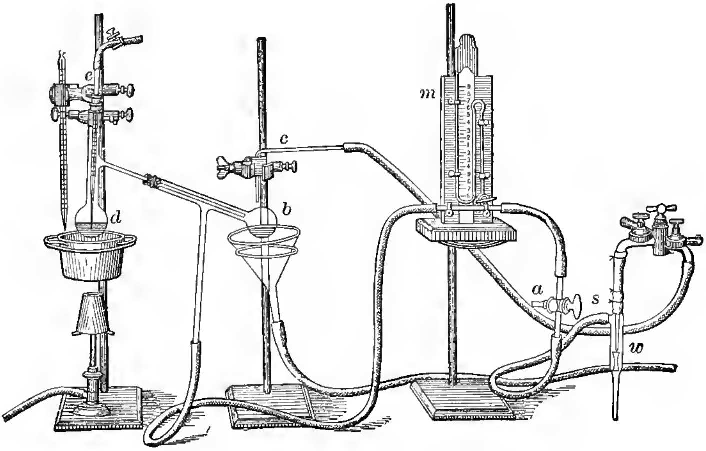


FIG. 12.—DISTILLATION IN VACUUM.

21. The separation of a mixture of volatile substances is effected by *fractional distillation*. If a mixture of two liquids, boiling, for example, at 100° and at 130°, is distilled, more of that boiling at 100° distils over at the beginning, and more of that boiling at 130° at the end, of the operation. If the distillate passing over below 110° is collected separately in one fraction, and similarly that between 120° and 130°, a rough separation is effected, while the middle fraction still consists of a mixture. To make the separation as complete as possible, the fraction 100°–110° is returned to the fractionation-flask and distilled till the thermometer reaches 110°, the fraction 110°–120° then mixed with the residue in the fractionation-flask, and the distillation then continued till the thermometer again stands at 110°. The receiver is changed, and the distillation renewed till the thermometer reaches 120°. The fraction 120°–130° is then added to the liquid in the distillation-flask, and the distillate collected in the same receiver, until the thermometer again indicates 120°. The portion distilling subsequently is collected separately. By several repetitions of this process it is possible often to effect an almost complete separation, it being usually advantageous to collect the fractions between narrower limits of temperature, and thus to increase their number.

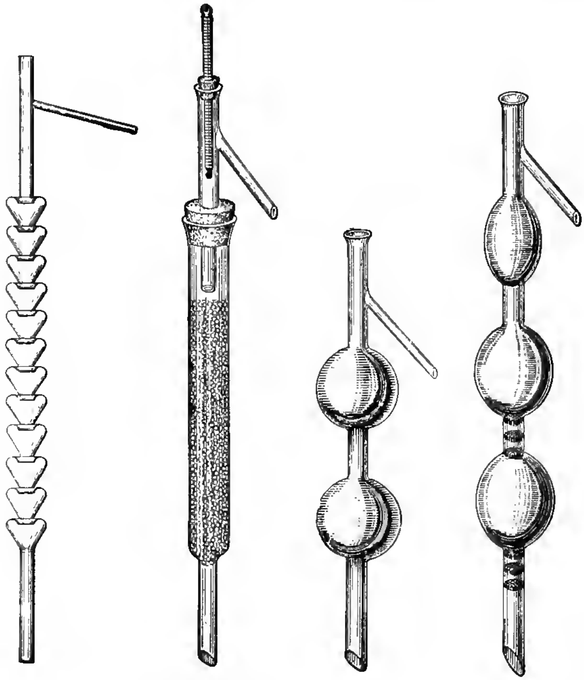

Young. Hempel. Wurtz. Linneman.

FIG. 13.—FRACTIONATING-COLUMNS.

The separation is much facilitated by using a fractionating-column (Fig. 13) connected to the neck of the boiling-flask:

the vapour of the least volatile constituents of the mixture is to a large extent condensed in the column. The stream of vapour from the distillation-flask heats the liquid in the fractionating-column, the effect being to vaporize its more volatile part, and simultaneously to condense the higher-boiling constituent of the vapour issuing from the flask.

22. A change in the composition of most liquid mixtures does not occasion a proportional alteration in their properties, like that expressed in the annexed graphic representation (Fig. 14) by a straight line *AB*. The abscissæ correspond with the molecular-percentage composition of the mixtures: the points *A* and *B* on the ordinates give the values of such physical constants as vapour-tension, boiling-point, specific gravity, etc., for the pure substances *A* and *B*, and the line *AB* the values of these constants for mixtures. The curve thus obtained usually varies more or less from a straight line.

The boiling-points of mixtures will be lower (line *c*) or higher (line *b*) than those calculated by the proportion-rule. Sometimes, these boiling-point curves will depart so much from the straight line as to show such maxima and minima as the curves *a* and *d*. Complete separation of such mixtures by fractional distillation at constant pressure is impossible, but is feasible when the boiling-point curves follow the course indicated by *b* or *c*. The most volatile, or lowest boiling, constituent of a mixture always distils first, so that the vapour is richer in *A* and the residual liquid in *B*. If the pure constituents *A* and *B* are more, or less, volatile than any mixture of the two, as represented by the boiling-point curves *b* and *c*, continued fractional distillation must lead to an approximately complete separation of *A* and *B*. But if the boiling-point curve has a maximum or minimum, the mixtures corresponding with it will consist of the most, or least, volatile constituents. On distillation, a fraction with this highest, or lowest, boiling-point will always be obtained, and at constant pressure further separation will be impossible.

Comprehension of this phenomenon will be facilitated by considering a boiling-point curve *b* without a maximum or minimum (Fig. 15). Since the most volatile portion of any mixture always volatilizes first, the vapour evolved from a boiling liquid always contains more of *A* than the liquid itself. When the composition of the mixture is *b*, that of the liquid will be *b′*. The *vapour-tension* *curve Ab′B* throughout the complete trajectory *AB* lies higher than the boiling-point curve (118).

If the boiling-point curve has a maximum *b* (Fig. 16), along the trajectory *Ab* the vapour will be richer in *A* than the liquid from which it is evolved: along the trajectory *bB* the vapour will contain more of *B* than the liquid, since *B* is now the most volatile, or lowest boiling, constituent. It follows that at the maximum *b* the vapour must have exactly the same composition as the liquid; that is, the mixture with maximum boiling-point distils at a constant temperature as though it were a single substance. For a mixture of liquids with a minimum boiling-point analogous results are

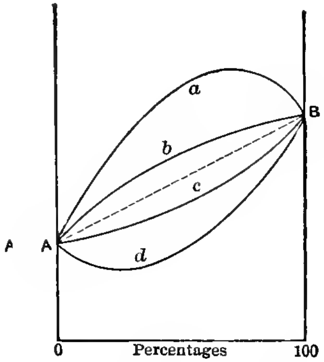


Fig. 14.

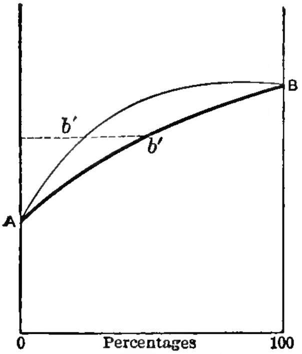


Fig. 15.

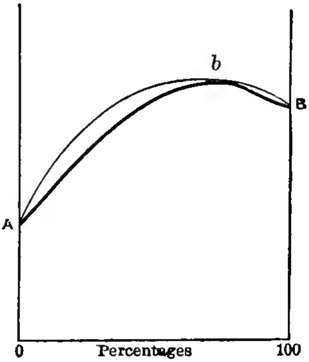


Fig. 16.

Fractional-distillation Curves.

obtained, so that in the graphic representation the vapour-tension curve must be tangential to the boiling-point curve, and touch it at the minimum-point.

The separation of a mixture of liquids by fractionation is also impossible when the boiling-points of its constituents are close together, because the essential characteristic of the whole method consists in the unequal volatility of the portions composing the mixture, resulting in the distillation of one substance before the other. If, however, the substances have nearly the same boiling-point, then both attain a vapour-tension of one atmosphere at almost the same temperature; in other words, they are almost equally volatile. With these conditions it is therefore impossible to apply the method successfully.

23. *Steam-distillation.* — In the preparation of many organic substances a crude reaction-product is often obtained containing tarry matter along with the required compound. To free the substance from this, use is often very advantageously made of the property possessed by many substances of distilling in a current of steam, the tarry matter remaining behind. Fig. 17 shows the apparatus employed in such a distillation.

Water is boiled in the can *a*, fitted with a delivery-tube *c* and a safety-tube *b*, the evolved steam being passed into the bottom of the distillation-flask *d*. If the distillation is interrupted, cooling causes diminished pressure in *a*, air being then able to enter the tube *b*. If *b* were not used, the liquid in *d* would flow back into *a*, owing to the fall in the steam-pressure.

Steam-distillation is also of service in separating compounds volatile with steam from others not volatile. With substances insoluble in water, the distillate is a milky liquid, because the water in the receiver is mixed with fine, oily drops. There is also an oily layer above or below the water.

In steam-distillations two liquids take part—water and the substance to be distilled. Usually these liquids are not miscible in all proportions. In the limiting case, when each liquid is wholly insoluble in the other, the vapour-pressure of each is unaffected by the presence of the other. At the boiling-point of the mixture, the sum of the vapour-pressures of the two constituents must be equal to the barometric pressure, since the liquid is boiling. The boiling-point must be lower than that at ordinary pressure of the lower-boiling of the two substances, because the partial pressure is necessarily smaller than the total pressure, which is equal to that of the atmosphere. The same result is therefore attained as by distillation at diminished pressure; that is, the volatilization of the substance at a temperature lower than its boiling-point under ordinary pressure.

Whether a substance distils quickly or slowly with steam depends on its partial pressure and on its vapour-density, together with the values of these physical constants for water. If the pressures are p_1 and p_2, and the vapour-densities d_1 and d_2, the quantities distilling simultaneously are p_1d_1 (substance) and p_2d_2 (water). If the ratio $p_1d_1 : p_2d_2$ is large, the substance distils with a small quantity of water, the distillation being quickly completed. The reverse takes place when the ratio $p_1d_1 : p_2d_2$ is small.

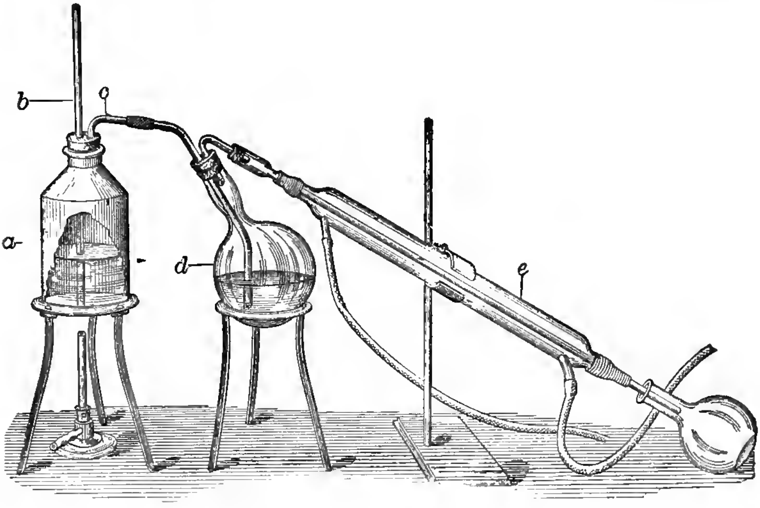


FIG. 17.—STEAM-DISTILLATION.

JAMES WALKER gives the following example. At a pressure of 760 mm. a mixture of nitrobenzene and water boils at 99° The steam exerts a pressure of 733 mm., so that the tension of the nitrobenzene-vapour is 27 mm. Since the vapour-densities of water and nitrobenzene are in the ratio of their respective molecular weights, 18 and 123, the proportion of water to nitrobenzene in the distillate should be as $733 \times 18 : 27 \times 123$; that is, approximately as 4:1. Notwithstanding its small vapour-tension at the boiling-point of the mixture, the quantity of nitrobenzene which passes over is about one-fifth of the total distillate, the rapid volatilization of the nitrobenzene being due to the fact that it has a large, and water a small, molecular weight. Even when an organic compound under similar conditions has a vapour-tension of only 10 mm., it distils with steam sufficiently rapidly to render the method applicable to its purification.

24. *Separation of Two Immiscible Liquids.*—For this purpose, a *separating-funnel* (Fig. 18) is employed: the method can be inferred from the drawing without further explanation. It is also applied to the *extraction* of aqueous solutions of substances soluble in a volatile liquid immiscible with water, such as *ether, light petroleum, chloroform, carbon disulphide.* The solution is transferred to a separating-funnel; ether, if that solvent is selected, is added; and after the mouth of the funnel has been closed by a glass stopper, the two liquids are mixed together by vigorous shaking, whereupon the substance dissolved in the water passes partly into the ether. The ethereal solution is allowed to rise to the surface, and separated from the water by opening the stop-cock after removal of the stopper. The water dissolved by the ether during the shaking is removed by chloride of calcium, or some other drying agent, and finally the ether is distilled off. When the dissolved substance is only slightly soluble in water, and easily soluble in ether, the extraction is completed quickly: it is then possible to exhaust the aqueous solution almost completely by several repetitions of the process, using fresh ether for each extraction. Otherwise, the shaking must be repeatedly carried out, and even then the extraction is imperfect.

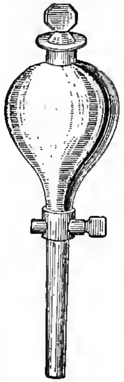


FIG. 18.—SEPARATING-FUNNEL.

When two immiscible solvents are simultaneously in contact with a substance soluble in both, the latter distributes itself so that the ratio of the concentrations reached in both solvents is constant (law of BERTHELOT). If a quantity X_0 of the substance is dissolved in a quantity l of the first solvent (water), and this solution extracted with a quantity m of the second solvent (ether), there will then remain a quantity X_1 in the first solution, so that X_0-X_1 has passed into the second solvent.

The value of the quantity X_1 is, in accordance with the above law, given by the equation

$$\frac{X_1}{l}=K\frac{X_0-X_1}{m} \quad \text{or} \quad X_1=X_0\frac{Kl}{m+Kl},$$

for $\frac{X_1}{l}$ and $\frac{X_0 - X_1}{m}$ are the two concentrations after agitation with the solvents, and K is the number expressing the constant ratio, or the *coefficient of distribution* (German, *Teilungskoeffizient*).

A second extraction with the same quantity m of the second solvent gives

$$\frac{X_2}{l} = K\frac{X_1 - X_2}{m},$$

or, substituting the value of X_1 from the first equation,

$$X_2 = X_0\left(\frac{Kl}{m + Kl}\right)^2,$$

and for the nth extraction,

$$X_n = X_0\left(\frac{Kl}{m + Kl}\right)^n.$$

Thus X_n, the quantity remaining in the first solvent (water), diminishes as n increases, and as m and K are respectively greater and less. Complete extraction is impossible, because although $\left(\frac{Kl}{m + Kl}\right)^n$ can approach zero very closely, it can never become equal to it.

Examples will facilitate comprehension of this formula. Suppose the problem is to determine how often 1000 c.c. of an aqueous solution of benzoïc acid must be extracted with 200 c.c. of ether to remove all the benzoïc acid from the solution. In this instance $l = 1000$ c.c., and $m = 200$ c.c. By experiment K is found to have approximately the value $\frac{1}{80}$; that is, if the concentration of the benzoïc acid in the ethereal solution is represented by 80, that in the aqueous solution is expressed by 1. On substituting these values for l, m, and K respectively, the formula becomes

$$\frac{X}{X_0} = \frac{Kl}{m + Kl} = \frac{1000 \times \frac{1}{80}}{200 + 1000 \times \frac{1}{80}} = \frac{1}{17},$$

which means that a single extraction with 200 c.c. of ether leaves $\frac{1}{17}$ of the benzoïc acid in the aqueous solution. After three extractions with 200 c.c. of ether, there remains only $\left(\frac{1}{17}\right)^3 = \frac{1}{4913}$ of the acid, so that the extraction of the acid is practically complete.

For succinic acid $K = 6$. A single extraction of 1000 c.c. of an aqueous solution of this acid with 200 c.c. of ether leaves $\frac{6000}{200+6000}=\frac{30}{31}$ of the acid still dissolved in the water. Repeated extraction is necessary to remove all the succinic acid from the aqueous solution.

It can be further shown from the equation by the use of the differential calculus that with a given quantity of the second solvent (ether) a more complete separation is effected by extracting frequently with small quantities than by using larger quantities a correspondingly fewer number of times.

Separation of Solids and Liquids.—This is effected by filtration, a process materially accelerated by attaching the funnel with a rubber stopper to a flask *a* (Fig. 19), connected through *b* to a water air-pump. To prevent rupture of the point of the filter-paper, it must be supported by a hollow platinum cone *c*.

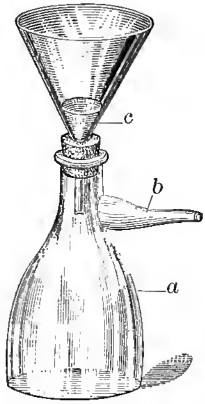


FIG 19.—FILTERING-FLASK.

25. *Separation of Solids from one Another.*—This process depends on difference in solubility. For a soluble and an insoluble substance the operation is very simple. If both substances are soluble, the method of *fractional crystallization* must be used. The mixture is dissolved in the minimum quantity of a boiling liquid: on cooling the solution the less soluble substance crystallizes first. The mother-liquor is poured off just as crystals of the second body begin to separate, and the second compound crystallized either by further cooling or by concentrating the liquid by evaporation. Several repetitions of these processes are essential to the separation. Even when the pure compounds have very different solubilities, the method is not free from difficulty, because the solubility of one substance may be very considerably modified by the presence of another. Water, alcohol, ether, glacial acetic acid, benzene, and other substances are employed as solvents.

26. From the foregoing it is seen that solid substances are usually purified by crystallization, and liquids by distillation. It is an *indication of purity* when the physical constants remain unchanged after the substance has been purified anew. Although

every physical constant could serve this purpose, the *melting-point* and the *boiling-point* are those most used, because they are easily determined, and slight impurities exercise a very material influence upon them. They also often afford a means of identifying substances. If a compound has been obtained by some process and is supposed to be one already known, it is strong evidence in favour of the supposition if the melting-point and boiling-point of the substance coincide with those of the compound with which it is supposed to be identical. For this reason determinations of melting-points and boiling-points are very often carried out.

The best method of ascertaining whether two substances are identical is to mix them in approximately equal proportions and determine the melting-point of the mixture. When identity exists, the melting-point of the mixture will coincide with that of the two individual substances; when it does not, the mixture melts at a much lower temperature, which is not sharply defined.

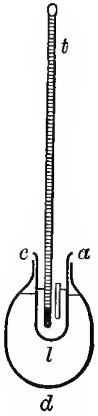


FIG. 20.—DETERMINATION OF THE MELTING-POINT.

To determine the *melting-point*, the substance is placed in a narrow thin-walled small tube sealed at one end (Fig. 20). This tube is attached to a thermometer *t*, the bulb of which dips into a liquid of high boiling-point, such as concentrated sulphuric acid or liquid paraffin (33), the viscosity of either causing the small tube to adhere to the thermometer. The tube *alc*, surrounding the bulb of the thermometer and the little tube, is loosely fixed in a small round glass flask *adc*, containing the same liquid as the tube *alc*. When *adc* is heated, the contents of the tube *alc* are, warmed uniformly, and the moment of fusion of the substance. at which the thermometer is read, can be very accurately observed.

The *boiling-point* is determined by heating the liquid to boiling in a fractionation-flask with a high side-tube. Short thermometers are used, so that the whole of the mercury column is surrounded by the vapour of the boiling liquid. To avoid inconveniently small graduations, these thermometers are constructed so that they can only be employed for a comparatively small range of temperature, six or seven different instruments being used for temperatures between 0° and 360°. These are called "abbreviated" thermometers.

27. Sometimes physical constants other than the melting-points and boiling-points are determined in the investigation of organic compounds. 1. The *specific gravity* can be determined with the *pyknometer*, the most useful form of which is shown in Fig. 21. It consists of two thick-walled capillaries *ab* and *cd*, terminating in a wider tube *bc*. The parts *aa* and *dd* are furnished with a millimetre-scale. The capacity of the apparatus is first determined, as well as that of the space between two divisions, by filling it several times up to different divisions with water of known temperature, and then weighing. The liquid under investigation is then placed in the apparatus, and this is weighed after the positions of the menisci in the capillaries have been observed; from the *data* thus obtained the specific gravity can be calculated.

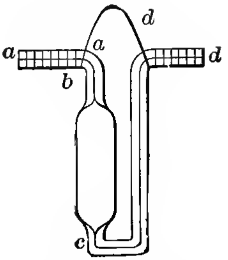


FIG. 21.—PYKNOMETER.

2. The rotation of the *plane of polarization* is another constant of importance.

Some substances, such as turpentine, a solution of sugar, etc., have the property of *rotating* out of its original position the plane of a ray of polarized light passing through them. This phenomenon is called the *rotation of the plane of polarization*, and substances possessing this property are said to be *optically active*. *Polarimeters* have been constructed for measuring the angle through which the plane of polarization has been rotated by an optically active substance: of these LAURENT'S (Fig. 22) is one of the best known. The yellow sodium-light of the burner *TT* is polarized in the part of the apparatus marked *BD*, and then passes through a tube of known length (200–500 mm.) placed in the channel *L*. This tube contains the liquid or solution under examination. The part *OC* of the apparatus serves to measure the rotation of the plane of polarization.

The extent to which the plane of polarization is rotated is proportional to the length of the tube, and is variously expressed. The rotation of a substance can be stated, for example, in terms of the effect produced by a given length of the tube described. The angle of rotation is read off directly from the instrument, and is usually denoted by α. By convention, the *specific rotatory power* is defined as the quotient obtained by dividing α by the product of the length of the tube into the specific gravity of the liquid. This value is denoted by $[\alpha]$, so that

$$[\alpha] = \frac{\alpha}{ld},$$

where l is the length of the tube, and d the specific gravity of the liquid. Under these conditions, $[\alpha]$ expresses the rotatory power of a substance per unit length of the tube (1 decimetre), and for unit weight of the substance divided into the unit of volume.

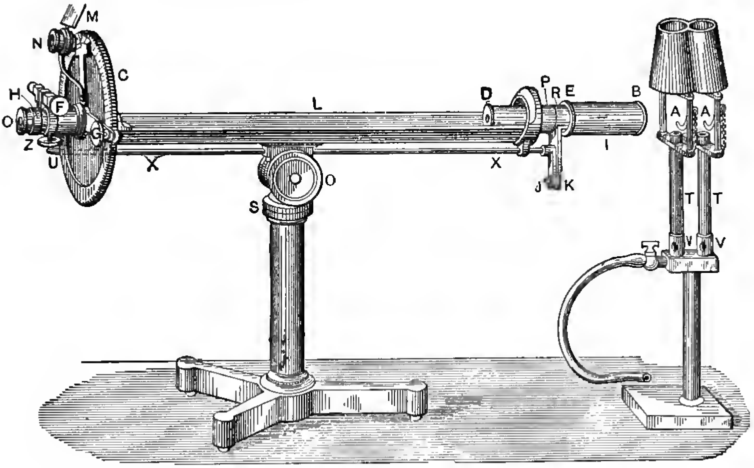


Fig. 22.—Laurent's Polarimeter.

The extent of the rotation is dependent on the colour of the light. The measurement is often carried out with sodium-light, which gives a yellow line in the spectroscope, denoted by D. This is expressed by the symbol $[\alpha]_D$.

When the rotatory power of a substance is small, or when, on account of its slight solubility, it can only be obtained in dilute solution, the rotation can often be increased by adding a solution of boric acid, molybdic acid, uranium salts, or other substances. The cause of this phenomenon is not fully understood.

It is often important to determine constants, such as the *index of refraction*, the *molecular electric conductivity*, the *heat of combustion*, and others.

CLASSIFICATION OF ORGANIC COMPOUNDS.

28. The organic compounds are very numerous. They are usually classed in two main divisions. One of these includes the *fatty* or *aliphatic compounds,* and the other the *aromatic compounds.* The first owes its name to the fact that the animal and vegetable fats belong to it; the second, to its containing many compounds, among the first to be discovered in this division, characterized by an agreeable smell or aroma.

The aliphatic compounds and the aromatic compounds are regarded as being derived from methane, CH_4, and benzene, C_6H_6, or compounds related to them, respectively.

It will be shown later that there are important differences between the general properties of these two classes of compounds.

FIRST PART.

THE ALIPHATIC COMPOUNDS.

SATURATED HYDROCARBONS.

29. The aliphatic compounds are defined in **28** as those derived from *methane*, CH_4. It is, therefore, advisable to begin the study of these compounds with this hydrocarbon.

Methane occurs in nature in the gases evolved from volcanoes. It escapes in coal-mines during the working of the coal-seams, and is called *fire-damp* by the miners. It is also called *marsh-gas*, being present in the gases evolved from marshes by decay of vegetable matter. It is an important constituent of coal-gas, being present to the extent of 30–40 per cent.

It can be obtained by the following methods.

1. By BERTHELOT's synthesis. A mixture of H_2S and CS_2 is led over red-hot copper contained in a tube, when the following reaction ensues:

$$2H_2S + CS_2 + 4Cu = 4CuS + CH_4.$$

2. By SABATIER and SENDERENS's synthesis. When a mixture of hydrogen and carbon monoxide is passed over reduced nickel at 250°–300°, methane is formed:

$$CO + 3H_2 = CH_4 + H_2O.$$

The nickel undergoes no apparent change, and can be used repeatedly. At a temperature of 230°–300°, carbon dioxide reacts similarly with hydrogen in presence of finely-divided nickel:

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

Since CS_2, H_2S, CO, and CO_2 can be obtained by direct synthesis from their elements, these reactions furnish methods of preparing methane synthetically.

Methane can also be synthesized directly from its elements by passing hydrogen through a heated tube containing reduced nickel mixed with very finely-divided carbon obtained by previously decomposing methane. An equilibrium is attained, corresponding at 475° and one atmosphere with 51 per cent. of methane:

$$CH_4 \rightleftarrows C + 2H_2.$$

3. By the action of water on aluminium carbide:

$$C_3Al_4 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

Other methods of preparation are referred to in **82** and **89.**

30. *Physical and Chemical Properties.*—Methane is an odourless and colourless gas of sp. gr. 0·559 (air = 1), liquefying at 11° and 180 atmospheres. It boils at −160°, and solidifies at −186°. It is only slightly soluble in water, but more so in alcohol. It is decomposed into carbon and hydrogen by the sparks of an induction-coil, or in the electric arc. Oxidizing substances, such as nitric and chromic acids, do not attack it, or only very slightly, while concentrated sulphuric acid and strong alkalis have no action upon it. It burns with an almost non-luminous flame. When mixed with air or oxygen it forms a violently explosive mixture, the reaction being in accordance with the equation

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

This so-called "fire-damp" is the cause of the explosions which sometimes occur in coal-mines. Chlorine and bromine react with methane, replacing its hydrogen atoms by halogen atoms, and forming a hydrogen halide:

$$CH_4 + 2Cl = CH_3Cl + HCl.$$

The replacement of one atom by another is called *substitution.* If chlorine or bromine is present in excess, the final product is CCl_4 or CBr_4.

31. There exists a series of hydrocarbons having general chemical properties similar to those of methane. Examples of these compounds are *ethane* C_2H_6, *propane* C_3H_8, *butane* C_4H_{10}, *pentane* C_5H_{12}, *hexane* C_6H_{14}, etc., *pentatriacontane* $C_{35}H_{72}$, and *hexacontane* $C_{60}H_{122}$. These formulæ can be summed up in the general expression C_nH_{2n+2}: for methane, $n = 1$. The hydrocarbons C_nH_{2n+2} resemble methane in their power of resisting oxidation,

and are unacted on by concentrated sulphuric acid, while halogens act on them with substitution of hydrogen and formation of compounds $C_nH_{2n+1}Cl$, $C_nH_{2n}Cl_2$, and so on.

The higher hydrocarbons can be obtained by building-up from those lower in the series. For example, ethane is got from methane by replacement of a hydrogen atom by halogen, and treatment of the halide thus obtained with sodium or calcium:

$$2CH_3I + Na_2 = C_2H_6 + 2NaI.$$

Propane can be prepared in accordance with tne following equation:

$$CH_3I + C_2H_5I + Na_2 = C_3H_8 + 2NaI:$$

and, in general, C_nH_{2n+2} is obtained by the action of sodium upon $C_mH_{2m+1}I + C_pH_{2p+1}I$, when $m+p=n$.

In addition to propane, butane, C_4H_{10}, is formed from $2C_2H_5I$, and ethane, C_2H_6, from $2CH_3I$, three hydrocarbons being obtained. This is always so in such syntheses.

Since methane can be prepared synthetically, it is evidently possible to synthesize each hydrocarbon of the formula C_nH_{2n+2}.

32. *Nomenclature.*—The hydrocarbons C_nH_{2n+2} are always denoted by the termination "ane." The first four members, methane, ethane, propane, and butane, have special names: the others are denoted by the Greek or Latin numeral corresponding with the number of carbon atoms. Thus C_8H_{18} is called *octane*, $C_{12}H_{26}$ *dodecane*, $C_{31}H_{64}$ *hentriacontane*, and so on.

It will often be necessary to consider groups of atoms unobtainable in the free state, but theoretically derivable by removal of a hydrogen atom from the hydrocarbons C_nH_{2n+2}. These groups have the general formula C_nH_{2n+1}, and are called *alkyl-groups*. They are denoted individually by changing the termination "ane" of the corresponding hydrocarbon into "yl." Thus CH_3 is called *methyl*, C_2H_5 *ethyl*, C_3H_7 *propyl*, C_4H_9 *butyl*, $C_{12}H_{25}$ *dodecyl*, etc.

The hydrocarbons C_nH_{2n+2} have the general name *saturated hydrocarbons*, because they are saturated with hydrogen; that is, are unable to take up any more hydrogen atoms into the molecule. They are also called *paraffins*, because paraffin-wax consists of a mixture of the higher members. The word paraffin is derived from *parum affinis*, and indicates the stability of this substance towards chemical reagents.

33. *Occurrence in Nature.*—The hydrocarbons C_nH_{2n+2} occur in nature in enormous quantities. Crude American petroleum consists of a mixture of a great number of these compounds, from the lowest to the highest members of the series. Three principal products are obtained from this petroleum by fractional distillation, after treatment with acids and alkalis to free it from substances other than hydrocarbons of the formula C_nH_{2n+2}. The most volatile portion is called *light petroleum, petroleum-ether, benzine, naphtha,* or *ligroïn:* it distils between 40° and 150°, and contains lower members, chiefly C_6H_{14}, C_7H_{16}, and C_8H_{18}. It is extensively employed as a solvent for fats, oils, and resins, and is also applied to the removal of stains from clothing in the "dry-cleaning process."

The portion distilling between 150°–300° is ordinary *petroleum,* and is used on a large scale for lighting and cooking.

The danger involved in its use is by no means small, a large number of accidents by fire being attributable to this source. The fact that fires are often caused by the overturning of petroleum-lamps is traceable to the presence in the petroleum of a part of the more volatile products, and to their vapour producing an inflammable mixture with air. When a lamp filled with petroleum freed by careful fractionation from constituents of low boiling-point, is upset, the flame is extinguished. Petroleum thus purified is a commercial product.

To ascertain whether a sample of petroleum contains these more volatile products, its *flash-point* is determined by heating it slowly in a specially constructed apparatus, devised by Sir FREDERICK ABEL, and observing the temperature at which the mixture of vapour and air over the petroleum can just be ignited. Experience has shown that there is no danger with a flash-point of 40° C. (104° F.). Large quantities of petroleum come into the market with a flash-point of 22°–24° C. (72°–75° F.): they are the cheaper kinds, are used by the largest proportion of the population, and constitute a great source of danger from fire. It would be very advantageous if the law insisted upon a flash-point of about 40° C. or 104° F., as has already been done in some countries.

The portion of the crude petroleum which does not distil below 300°, but remains in the still, is named "vaseline." It is semi-solid at ordinary temperatures, white when pure, and is used in pharmacy in the preparation of ointments. It is further employed for covering the surface of metallic articles to protect them from oxidation, for this purpose being better than fat, because the latter turns sour and then attacks the surface of the metal, whereas vaseline has a neutral reaction, and remains unchanged in the air.

As already mentioned, *paraffin-wax* is a mixture of the highest members of the series C_nH_{2n+2}. Some kinds of crude petroleum, notably that obtained from Java, contain considerable quantities of these highest members. They are present in but small amount in American petroleum.

Liquid paraffin is a product of high boiling-point, obtained in the dry distillation of brown coal.

Earth-wax, or *ozokerite*, occurs in Galicia, and consists chiefly of paraffin. This substance is also obtained in the dry distillation of the brown coal found in Saxony.

34. Petroleum has probably been formed from fats under the influence of high temperature combined with great pressure, ENGLER having obtained a liquid very similar to American petroleum by distilling these substances under increased pressure. Opinion is divided concerning the origin of these fats. According to some, they come from fish; but it is difficult to understand how the enormous quantities of petroleum found in some places could have this origin. Another explanation attributes its formation to very small organisms, called *diatoms:* they were present in enormous numbers in the earlier geological periods. They produced a sort of wax, and it yielded petroleum when distilled under pressure.

Another hypothesis has been suggested by MOISSAN. It attributes the formation of petroleum to the action of water on certain metallic carbides formed by the intense heat of volcanoes. On treatment with water, most of these carbides yield gaseous hydrocarbons, principally methane and acetylene. But when these hydrocarbons are exposed to a high temperature and pressure they are converted into a liquid resembling petroleum, the change being much facilitated by the presence of hydrogen, and by the catalytic influence of finely-divided metals, such as iron or nickel. SABATIER and SENDERENS have thus been able, by varying the experimental conditions, to prepare specimens of synthetical petroleum resembling the natural products of the Caucasus, Galicia, and America.

Homologous Series.

35. Each of the hydrocarbons C_nH_{2n+2} differs in composition from the rest by $n \times CH_2$, as the general formula shows. It was pointed out (31) that this difference exercises but slight influence on their chemical properties.

Whenever organic compounds show great resemblance in their chemical properties, and have at the same time a difference in composition of $n \times CH_2$, they are said to be *homologous*, the name *homologous series* being given to such a group of compounds. As will be seen later, many of these series are known.

It is easy to understand how much this simplifies the study of organic chemistry. Instead of having to consider the chemical properties of each compound individually, it is sufficient to do so for one member of a homologous series, as this gives the principal characteristics of all the other members. In addition to the main properties common to the members of a homologous series, each individual member has its characteristics. Except in a few instances, this book will not deal with the latter, because they only need to be considered in a more extensive survey of the subject.

36. The *physical properties*, such as the melting-points and boiling-points, specific gravities, and solubilities, of the members of a homologous series, generally change uniformly as the number of carbon atoms increases. In general it may be said that the melting-points and boiling-points rise from the lower to the higher members of a homologous series.

A table of some of the physical constants of a number of normal (40) members of the paraffin series is given on p. 41.

An inspection of this table reveals that the first four members are gases at the ordinary temperature, those from C_5 to C_{16} liquids, and the higher members solids. Although methane is odourless, the liquid members have a characteristic petroleum-like smell; the solid members, on the other hand, are odourless. All are nearly insoluble in water.

It should be further remarked that the differences between the melting-points and boiling-points respectively of successive members of the series become smaller with increase in the number of carbon atoms. This phenomenon is usually found in homologous series.

Formula.	Name.	Melting-point.	Observed Boiling-point.	Calculat'd Boiling-point.	Specific Gravity.
CH_4	Methane	−186°	−160°	−166·3°	0·415 (at −160°)
C_2H_6	Ethane	−172·1°	− 93°	− 95·3°	0·446 (at 0°)
C_3H_8	Propane	——	− 45°	− 43·1°	0·536 (at 0°)
C_4H_{10}	Butane	——	1°	− 0·4°	0·600 (at 0°)
C_5H_{12}	Pentane	——	36·4°	36·4°	0·627 (at 14°)
C_6H_{14}	Hexane	——	68·9°	68·9°	0·658 (at 20°)
C_7H_{16}	Heptane	——	98·4°	98·3°	0·683 " "
C_8H_{18}	Octane	——	125·6°	125·1°	0·702 " "
C_9H_{20}	Nonane	− 51°	149·5°	149·8°	0·718 " "
$C_{10}H_{22}$	Decane	− 31°	173°	172·8°	0·730 " "
$C_{11}H_{24}$	Undecane	− 26°	194°	194·3°	0·774 at melting-point
$C_{12}H_{26}$	Dodecane	− 12°	214·5°	214·6°	0·773 " "
$C_{14}H_{30}$	Tetradecane	4°	252·5°	252·0°	0·775 " "
$C_{16}H_{34}$	Hexadecane	18°	287·5°	285·9°	0·775 " "
$C_{20}H_{42}$	Eicosane	36·5°	205° *	——	0·7775" "
$C_{21}H_{44}$	Heneicosane	40·1°	215°	——	0·7778" "
$C_{23}H_{48}$	Tricosane	47·4°	234°	——	0·7799' "
$C_{31}H_{64}$	Hentriacontane	68·4°	302°	——	0·7799" "
$C_{35}H_{72}$	Pentatriacontane	74°	331°	——	0·7813" "
$C_{60}H_{122}$	Hexacontane	101°	——	——	——

* At 15 mm. pressure, and the same for those following.

For the boiling-points these differences are functions of the absolute temperature. SYDNEY YOUNG has induced the empirical formula

$$\varDelta = \frac{144 \cdot 86}{T^{0 \cdot 0148\sqrt{T}}},$$

giving the difference in boiling-point of two successive members of the series, when T is the boiling-point on the absolute scale of the more volatile of the two homologues. The boiling-points in the fifth column of the table in this section were calculated by the aid of this formula.

The expression holds not only for this homologous series of hydrocarbons, but also for many other homologous series. The differences between the calculated and observed boiling-points are greatest for the lower members. For some homologous series the divergences are considerable, but can usually be proved to be due to association of the molecules of the compound in the liquid state; that is, the molecular weight in this condition is twice, or a higher multiple of, that in the normal gaseous state.

YOUNG's formula holds for normal pressure, 760 mm. For the absolute boiling-points of two substances a and b the simple relation

$$\frac{T_a}{T_b}=\frac{T'_a}{T'_b}$$

often obtains, T and T' being the absolute boiling-points of the substances at the same arbitrary pressure. Otherwise expressed, this equation means that the ratio of the boiling-points at different pressures is constant.

Isomerism and Structure.

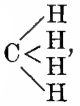
37. Only one substance with the formula CH_4 is known: it is methane. Similarly, there is only one compound having the formula C_2H_6, and one with the formula C_3H_8. There are known, however, two compounds with the formula C_4H_{10}, three with the formula C_5H_{12}, five with the formula C_6H_{14}, and so on. The phenomenon of two or more compounds being represented by one formula is called *isomerism* (2), and compounds having the same formula are called *isomerides*. Isomerism is explained by a consideration of the grouping of the atoms in the molecule.

One of two hypotheses may be adopted. In the first place, the arrangement of the atoms may be regarded as continually changing, a molecule being represented as like a planetary system, the configuration of which changes from moment to moment. This hypothesis, however, cannot explain the phenomenon of isomerism. For example, it is not apparent how the four carbon atoms and ten hydrogen atoms in butane could form two different substances if the arrangement were indeterminate, for there are trillions of molecules present in even one cubic millimetre, and all the possible configurations of these fourteen atoms must therefore be supposed to exist at any instant.

Isomerism can at once be understood by assuming a definite and unchanging arrangement of the atoms in the molecule, because the difference in the properties of isomeric compounds may be then explained by a difference in the arrangement of equal numbers of the same atoms.

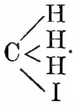
A definite and unchanging arrangement of the atoms in a molecule does not involve their being immovable with respect to one another. For example, they might revolve round a point of equilibrium without alteration in their order of succession.

38. Since the phenomenon of isomerism leads to the assumption of a definite arrangement of the atoms in the molecule, it is necessary to solve the problem of how the atoms in the molecules of different compounds are arranged. The basis of the solution is the quadrivalency of the carbon atom. In methane the arrangement of the atoms may be represented by the formula

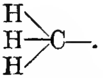


in which the four linkings of the carbon atom act, as it were, like four points of attraction, each holding a univalent hydrogen atom fast. This is the only possibility, because the hydrogen atoms cannot be bound to one another, the only point of attraction, or single linking, of each being already in union with one of the linkings of the carbon atom.

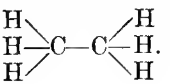
The arrangement of the atoms in ethane, C_2H_6, must now be investigated. This substance can be obtained by the action of sodium upon methyl iodide, CH_3I (59), with a quadrivalent carbon atom, three univalent hydrogen atoms, and one univalent iodine atom. It must therefore be represented thus:



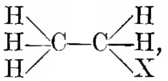
Sodium reacts with methyl iodide by withdrawing the iodine atoms from two molecules, with formation of ethane. The removal of the iodine atom has the effect of setting free the carbon linking previously attached to this atom, with the production of two groups



Since the formula of ethane is C_2H_6, it is evident that the only possible arrangement of its atoms is that having the two free linkings of the methyl-groups united to one another:

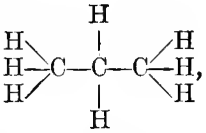


The arrangement of the atoms in propane can be determined in an exactly analogous manner. It was mentioned (**31**) that propane is formed by the action of sodium on a mixture of methyl and ethyl halides. Since ethane can be prepared by the action of sodium on methyl iodide, the formula of an ethyl halide can only be



where X represents a halogen atom.

If the halogen is taken away from this substance and from methyl iodide simultaneously, the residues unite, showing that propane has the structure



or shortly $H_3C \cdot CH_2 \cdot CH_3$.

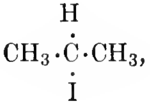
Such an arrangement of symbols expressing the configuration of a molecule, and indicating the form or structure, is called a *structural* or *constitutional formula.*

39. The following example makes it clear how cases of isomerism can be explained by differences in structure. One of the five known hexanes boils at 69°, and has a specific gravity of 0·6583 at 20·9°: another boils at 58°, and has a specific gravity of 0·6701 at 17·5°. The first is obtained by the action of sodium on *normal propyl iodide,* $CH_3 \cdot CH_2 \cdot CH_2I$. From the foregoing it follows that this hexane must have the structure

$$CH_3 \cdot CH_2 \cdot CH_2 — CH_2 \cdot CH_2 \cdot CH_3.$$

It is named *dipropyl,* on the assumption that it has been formed by the union of two propyl-groups.

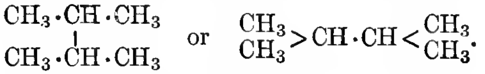
In addition to this normal propyl iodide, an isomeride called iso*propyl iodide* is known. Both compounds can be readily converted into propane, $CH_3 \cdot CH_2 \cdot CH_3$. Assuming that the isomerism is due to a different arrangement of the atoms in the molecule, it follows that the isomerism of the two compounds C_3H_7I can only be explained by a difference in the position occupied by the iodine atom in the molecule, because the arrangement of the atoms in propane is known, and the propyl iodides only differ from propane in having one of the hydrogen atoms in the latter replaced by iodine. *iso*Propyl iodide must therefore have the structure



$$CH_3\cdot\overset{\displaystyle H}{\underset{\displaystyle I}{\dot{C}}}\cdot CH_3,$$

if the constitution of normal propyl iodide is $CH_3\cdot CH_2\cdot CH_2I$.

The hexane boiling at 58° is produced by the action of sodium on *iso*propyl iodide, and consequently must have the structure



$$\begin{array}{c} CH_3\cdot CH\cdot CH_3 \\ | \\ CH_3\cdot CH\cdot CH_3 \end{array} \quad\text{or}\quad \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH<\!\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Hence it is called *di*iso*propyl.*

Carbon Chains.

40. The foregoing facts evidently make it reasonable to assume the existence of a bond between carbon atoms in the molecules of organic compounds. *This bond is a very strong one,* since the saturated hydrocarbons resist the action of powerful chemical reagents (31). The property possessed by carbon atoms of combining to form a series of many atoms, a *carbon chain,* like that in the hexanes above described, furnishes a marked distinction between them and the atoms of all the other elements which either have not this power, or have it only in a very inferior degree. The fact that the number of carbon compounds is so enormous is due to this property, in conjunction with the quadrivalency of the carbon atom.

A carbon chain like that in dipropyl is said to be *normal.* On the other hand, an example of a *branched* chain is furnished by di*iso*propyl. Each carbon atom in the normal chain is linked directly to not more than two others: in branched chains there are carbon atoms directly linked to three or four others. A normal-chain compound is usually denoted by putting *n* before its name; branched-chain compounds are often distinguished by the prefix *iso.*

A few other definitions may find a place here. A carbon atom linked to only one other carbon atom is called *primary;* if linked to two carbon atoms it is named *secondary;* if to three, *tertiary;* if to four, *quaternary.* A carbon atom situated at the end of a chain is called *terminal.* The carbon atoms of a chain are distinguished by numbers, the terminal one being denoted by **1**, the one next it by **2**, and so on; for example,

$$\underset{1}{CH_3}\cdot\underset{2}{CH_2}\cdot\underset{3}{CH_2}\cdot\underset{4}{CH_3}.$$

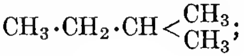
Sometimes the terminal atom is denoted by α, the one linked to it by β, and the succeeding one by γ, etc., but a terminal C-atom in a CN-group, CHO-group, or COOH-group, is distinguished by ω, the next by α, and so on.

Law of the Even Number of Atoms.—The number of hydrogen atoms in the saturated hydrocarbons is even, since their formula is C_nH_{2n+2}. All other organic compounds may be regarded as derived by exchange of these hydrogen atoms for other elements or groups of atoms, or by the removal of an even number of hydrogen atoms, or by both causes simultaneously. From this it follows that the sum of the atoms with uneven valency (hydrogen, the halogens, nitrogen, phosphorus, etc.) must always be an even number. The molecule of a substance of the empirical composition $C_3H_2O_2N$ must be at least twice as great as this, because 2H + 1N is uneven.

Number of Possible Isomerides.

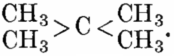
41. The quadrivalency of the carbon atom, coupled with the principle of the formation of chains of atoms, not only explains the existence of the known isomerides, but also renders possible the prediction of the existence of unknown compounds. Thus for a compound C_4H_{10} either the structure $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$ or $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH\cdot CH_3$ may be assumed, and there are no further possibilities. Pentane may have the following structural formulæ:

(1) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$; (2)



$$CH_3\cdot CH_2\cdot CH{<}\genfrac{}{}{0pt}{}{CH_3}{CH_3};$$

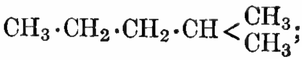
(3)



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{<}\genfrac{}{}{0pt}{}{CH_3}{CH_3}.$$

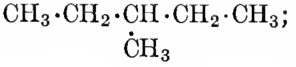
For hexane the following five are possible:

(1) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$; (2)



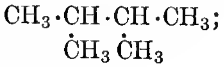
$CH_3\cdot CH_2\cdot CH_2\cdot CH<^{CH_3}_{CH_3}$;

(3)



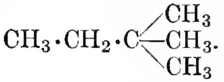
$CH_3\cdot CH_2\cdot \underset{CH_3}{CH}\cdot CH_2\cdot CH_3$;

(4)



$CH_3\cdot \underset{CH_3}{CH}\cdot \underset{CH_3}{CH}\cdot CH_3$;

(5)



$CH_3\cdot CH_2\cdot C\begin{smallmatrix}\diagup CH_3\\ -CH_3\\ \diagdown CH_3\end{smallmatrix}$.

If the principles given above be assumed, it will be impossible to find structural formulæ other than those mentioned.

Should it be possible actually to obtain the same number of isomerides as can be thus predicted, and no more, and should the products of synthesis or decomposition of any existing isomeride necessitate the assumption of the same structural formula as that required by the theory, these facts constitute a very important confirmation of the correctness of the principles upon which the theory is based. This correspondence of fact with theory has been proved to hold good in many instances, and therefore, on the other hand, affords an important means of determining the structure of a new compound, because if all the structural formulæ possible for the compound according to the theory are considered in turn, one of them will be found to be that of the substance.

Frequently the number of isomerides actually known is much smaller than that which is possible, because the number of possible isomerides increases very quickly with increase of the number of carbon atoms in the compound. Cayley has calculated that there are nine possible isomerides for C_7H_{16}, eighteen for C_8H_{18}, thirty-five for C_9H_{20}, seventy-five for $C_{10}H_{22}$, one hundred and fifty-nine for $C_{11}H_{24}$, three hundred and fifty-four for $C_{12}H_{26}$, eight hundred and two for $C_{13}H_{28}$, and so on. Chemists have not tried to prepare, for example, every one of the eight hundred and two possible isomerides of the formula $C_{13}H_{28}$, because their attention has been occupied by more important problems. There can, however, be no doubt as to the possibility of obtaining all these compounds, because, as mentioned above, the methods for building them up are known, and there would therefore be no theoretical difficulties in the way of these experiments, though there might be hindrances of an experimental nature.

Physical Properties of Isomeric Compounds.

42. Of the different isomerides the normal compound has the highest boiling-point; for the others the volatility increases with the number of side-chains. These rules are also applicable to other homologous series.

Boiling-points of the Isomeric Hexanes.

Normal hexane, $CH_3 \cdot (CH_2)_4 \cdot CH_3$: 69°.
Methyldiethylmethane, $(C_2H_5)_2CH \cdot CH_3$: 64°.
Ethyl*iso*butyl, $C_2H_5 \cdot CH_2CH(CH_3)_2$: 62°.
Di*iso*propyl, $(CH_3)_2CH \cdot CH(CH_3)_2$: 58°.
Trimethylethylmethane, $(CH_3)_3C \cdot C_2H_5$: 46°.

ALCOHOLS, $C_nH_{2n+2}O$.

Methods of Formation and Constitution.

43. The *alcohols* of this homologous series can be obtained by the action of silver hydroxide on the alkyl halides:

$$C_nH_{2n+1}I + AgOH = C_nH_{2n+2}O + AgI.$$

It is usual to bring an alkyl iodide into contact with moist oxide of silver, the portion dissolved in the water reacting like silver hydroxide ("Inorganic Chemistry," 246). The preparation of the alcohol from the iodide can also be effected by heating it with excess of water at 100°:

$$C_2H_5I + H_2O = C_2H_6O + HI.$$

When sodium reacts with an alcohol $C_nH_{2n+2}O$, one gramme-atom of free hydrogen is liberated from each gramme-molecule of the alcohol, and a compound called *sodium alkoxide* (*alcoholate*), $C_nH_{2n+1}NaO$, is produced: in presence of excess of water this decomposes into sodium hydroxide and an alcohol The sodium has thus replaced one atom of hydrogen, and neither it nor any other metal can replace more than one hydrogen atom: if excess of sodium is added, it remains unacted upon. It follows that only one hydrogen atom in the alcohol is replaceable by sodium.

When an alcohol is treated with trichloride or pentachloride of phosphorus, an alkyl chloride is formed:

$$3C_nH_{2n+2}O + PCl_3 = 3C_nH_{2n+1}Cl + H_3PO_3.$$

From these facts the constitution of the alcohols can be induced. Silver hydroxide can only have the structure Ag—O—H, its bivalent oxygen atom being linked to its univalent silver and hydrogen atoms. When silver hydroxide is brought into contact with an alkyl iodide, the reaction must be supposed to take place so that on the one hand the iodine atom is set free from the alkyl-group, and on the other hand the silver atom from the hydroxyl-group. The alkyl-group and the hydroxyl-group are thus afforded the opportunity of uniting by means of the linking set free in each:

$$C_nH_{2n+1}\boxed{I+Ag}OH \rightarrow C_nH_{2n+1}—OH.$$

This method of formation proves that the alcohols contain a hydroxyl-group. Their preparation from alkyl iodides and water leads also to the same conclusion, which is further supported by the two properties of alcohols mentioned on the last page. It is evident that if their structure is expressed by $C_nH_{2n+1}\cdot OH$, all the hydrogen atoms present, except one, are linked directly to carbon, while one hydrogen atom occupies a special position in the molecule, being attached to the oxygen atom, which is united through its second linking to a carbon atom. It is only natural to suppose that the special position occupied by this hydrogen atom is accompanied by a special property, that of being the only one of all the hydrogen atoms replaceable by alkali-metals. Moreover, sodium sets free hydrogen from another compound containing without doubt a hydroxyl-group: this compound is water, for which no other constitution is possible than H—O—H.

The fact that the alcohols are converted into alkyl chlorides by the action of the chlorides of phosphorus is additional proof that they contain a hydroxyl-group. The empirical formulæ $C_nH_{2n+2}O$ and $C_nH_{2n+1}X$ show that the halogen has replaced OH. It may be assumed that in this reaction the hydroxyl of the alcohol has changed places with the chlorine of the phosphorus compound:

$$3(C_nH_{2n+1}\cdot OH)+Cl_3P.$$

A consideration of the possible constitutional formulæ for substances having the general molecular formula $C_nH_{2n+2}O$ reveals the fact that the linkage of the oxygen atom admits of only two possible formulæ; thus, the compound C_2H_6O could be either

$$\text{I. } CH_3\cdot CH_2\cdot OH, \quad \text{or} \quad \text{II. } CH_3\cdot O\cdot CH_3.$$

Since all the hydrogen atoms in the second formula have the same value, it cannot be the one representing an alcohol, as it would not account for a very important property of these compounds, their interaction with the alkali-metals. The action of silver hydroxide on an alkyl iodide, or that of phosphorus chlorides on an alcohol, would accord equally ill with this formula, whereas formula I. explains these reactions fully. It must therefore be adopted.

The constitutional formulæ of the alcohols have thus been induced from their properties. Inversely, *the constitutional formulæ represent all the chemical properties of the compounds*, being simply a short way of expressing them. The value of these formulæ is evident: the structural formula of a compound, established by the study of some of its properties, reveals the rest of these properties. The existence of properties thus deduced has in many instances been established by experiment.

Nomenclature and Isomerism.

44. The alcohols of this series are named after the alkyl-groups contained in them; for example, *methyl alcohol, ethyl alcohol, propyl alcohol*, etc.

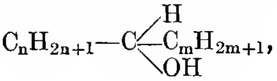
Isomerism may arise in three ways: by branching of the carbon chains; by changing the position of the hydroxyl-group; or through both these causes simultaneously.

This is seen from the following table of the isomeric alcohols C_3 to C_5.

Name.	Formula	Boiling-point.	Specific Gravity at 20° (d_4^{20}).
Propyl alcohols C_3H_8O			
1. Normal	$CH_3\cdot CH_2\cdot CH_2OH$	97°	0·804
2. *iso*	$CH_3\cdot CHOH\cdot CH_3$	81°	0·789
Butyl alcohols $C_4H_{10}O$			
1. Normal primary	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$	117°	0·810
2. „ secondary	$CH_3\cdot CH_2\cdot CHOH\cdot CH_3$	100°	
3. *iso*	$(CH_3)_2CH\cdot CH_2OH$	107°	0·806
4. Trimethylcarbinol	$(CH_3)_3C\cdot OH$	83°	0·786
Amyl alcohols $C_5H_{12}O$			
1. Normal primary	$CH_3\cdot (CH_2)_4\cdot CH_2OH$	138°	0·815
2. *iso*Butylcarbinol	$(CH_3)_2CH\cdot CH_2\cdot CH_2OH$	131°	0·810
3. Secondary butylcarbinol	$CH_3\cdot CH(C_2H_5)\cdot CH_2OH$	128°	
4. Methylpropylcarbinol	$CH_3\cdot (CH_2)_2\cdot CHOH\cdot CH_3$	119°	
5. Methyl*iso*propylcarbinol	$(CH_3)_2CH\cdot CHOH\cdot CH_3$	112·5°	
6. Diethylcarbinol	$C_2H_5\cdot CHOH\cdot C_2H_5$	117°	
7. Dimethylethylcarbinol	$(CH_3)_2C(OH)\cdot C_2H_5$	102°	
8. Tertiary butylcarbinol	$(CH_3)_3C\cdot CH_2OH$	112°	

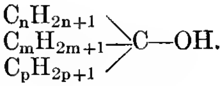
The alcohols with names ending in "carbinol" are so called because all alcohols may be looked upon as methyl alcohol (*carbinol*), in which one or more of the hydrogen atoms, with the exception of the one in the hydroxyl-group, are replaced by alkyl-groups (KOLBE). Thus, *iso*butyl alcohol is called iso*propylcarbinol*, secondary butyl alcohol *methylethylcarbinol*, normal butyl alcohol n-*propylcarbinol*, and so on.

The table also shows that in a *primary* alcohol the hydroxyl-group is linked to a primary carbon atom (40), and that in a *secondary* or a *tertiary* alcohol the hydroxyl is linked to a secondary or a tertiary carbon atom respectively. Similarly, any compounds which may be regarded as produced by replacement of hydrogen linked to a primary, secondary, or tertiary atom are called primary, secondary, or tertiary compounds. Primary alcohols are represented by the general formula $C_nH_{2n+1}—CH_2OH$, secondary by



$$C_nH_{2n+1}—C\begin{cases}H\\C_mH_{2m+1},\\OH\end{cases}$$

and tertiary by



$$\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\\C_pH_{2p+1}\end{matrix}\right\rangle C—OH.$$

General Properties of the Alcohols.

45. Some of the physical properties of the alcohols are given in this table, which includes only normal primary compounds.

Name.	Formula.	Specific Gravity d_0^0.	Boiling-point.	Difference of the Boiling-points.
Methyl alcohol	CH_3OH	0·812	66°	12°
Ethyl "	C_2H_5OH	0·806	78°	19°
Propyl "	C_3H_7OH	0·817	97°	20°
Butyl "	C_4H_9OH	0·823	117°	20°
Amyl "	$C_5H_{11}OH$	0·829	137°	20°
Hexyl "	$C_6H_{13}OH$	0·833	157°	18°
Heptyl "	$C_7H_{15}OH$	0·836	175°	16°
Octyl "	$C_8H_{17}OH$	0·839	191°	22°
Nonyl "	$C_9H_{19}OH$	0·842	213°	

This table, with that in 44, shows that the normal compounds have the highest boiling-points: this also holds for the hydrocarbons (42).

The lower alcohols (C_1-C_4) are mobile liquids, the middle members (C_5-C_{11}) are of a more oily nature, while the higher members are solid at the ordinary temperature. In thin layers all are colourless. In thick layers they are slightly yellow, the colour becoming more marked with increase in the number of carbon atoms. The first members (C_1-C_3) are miscible in all proportions with water, but the solubility of the higher members diminishes quickly as the number of carbon atoms increases.

The lower members have a spirituous, and those intermediate a disagreeable, smell; while the solid members are odourless. Their specific gravity is less than 1.

Methyl Alcohol, $CH_3 \cdot OH$.

46. *Methyl alcohol* is obtained on the large scale by the dry distillation of wood in iron retorts at as low a temperature as possible; or better, by treatment of wood with hot *producer-gas*, which is a mixture of carbon monoxide and nitrogen, obtained by passing air over coke at a white heat. To this method of preparation the substance owes its name *wood-spirit*. The products of the distillation are gases, an aqueous liquid, and tar. The aqueous solution contains 1–2 per cent. of methyl alcohol and a number of other substances, the chief being acetic acid (**89**) (*ca.* 10 per cent.) and acetone (**120**), (*ca.* 0.5 per cent.). The acetic acid is converted into calcium acetate by the action of lime, and the methyl alcohol purified by fractional distillation, and other methods. It is used in the arts in the preparation of aniline-dyes and formaldehyde, for the *denaturation* of spirit to render it unfit for drinking purposes (**48**), and in other processes.

Methyl alcohol burns with a pale-blue flame, and is miscible with water in all proportions, the mixing being accompanied by contraction and the development of heat. Its melting-point is $-93 \cdot 9°$. Its other physical properties are enumerated in the table in **45**.

Ethyl Alcohol, $C_2H_5 \cdot OH$.

47. *Ethyl alcohol*, or ordinary alcohol, is prepared artificially in enormous quantities. Its preparation depends upon a property possessed by *dextrose* (**209**), a sugar with the formula $C_6H_{12}O_6$, of decomposing into carbon dioxide and alcohol in presence of *yeast-cells:*

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

About 95 per cent. of the dextrose decomposes according to this equation. By-products such as *glycerol*, *succinic acid*, and other substances are also formed. Certain higher alcohols of this series, principally amyl alcohols, are also produced from the proteïns contained in the raw material (230).

On account of its cost, dextrose itself is not employed in the manufacture of alcohol, some substance rich in starch (223), $(C_6H_{10}O_5)_n$, such as potatoes, grain, etc., being used instead. By the action of *enzymes* (219), the starch is almost completely transformed into *maltose* (213), $C_{12}H_{22}O_{11}$, one molecule of this compound being then converted into two molecules of dextrose by the action of one molecule of water:

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose}}{2C_6H_{12}O_6}.$$

The enzyme employed in the technical manufacture of maltose from starch is called *diastase*, and is present in malt. The reaction it induces is called *saccharification*. When potatoes are used, they are first made into a thin, homogeneous pulp by treatment with steam under pressure at 140° to 150°, malt being added after cooling. At a temperature of 60° to 62°, the decomposition into maltose is completed in twenty minutes.

Yeast is then added to the maltose solution, and the fermentation carried on at a temperature below 33°. To separate the resulting alcohol from the other substances present, the product is submitted to distillation; and by using a *fractionating-column* (Fig. 23), alcohol of 90 per cent. strength can be obtained, although the concentration of the alcohol in the fermented liquid does not exceed 18 per cent.

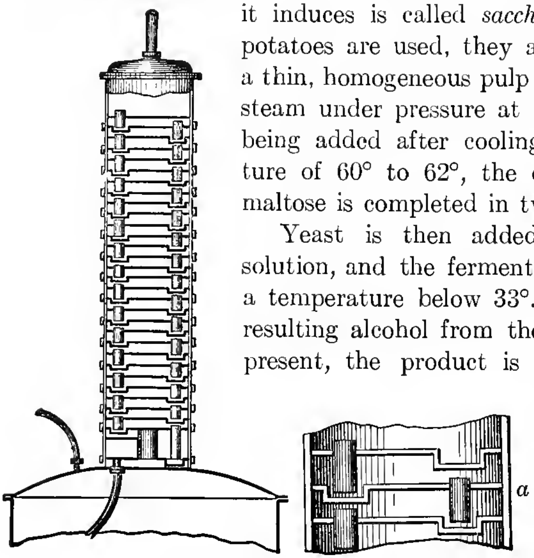


FIG. 23.—FRACTIONATING-COLUMN.

The thin liquid residue remaining in the still is called *spent wash,* and is used for feeding cattle. It contains, amongst other products, almost all the proteïns present in the material from which the spirit has been manufactured.

The crude spirit (*low wines*) so prepared is again carefully fractionated, when alcohol of 96 per cent. by volume (*spirits*) is obtained. The fractions of higher boiling-point consist of an oily liquid of unpleasant odour, called *fusel-oil:* it contains chiefly amyl alcohols and other homologues. The residue is called *spent lees.*

Alcoholic beverages are classified into those that have been distilled, and those that have not.

Distilled (about 50 per cent. of alcohol).	Not distilled.
Brandy or *cognac*, from wine.	*Beer*, from fermented malt and hops (3–7 per cent. of alcohol).
Whisky, from fermented solution of malt.	*Wine*, fermented grape-juice (8–17 per cent. of alcohol).
Rum, from fermented solution of sugar.	"*Fortified*" *wines*, such as *port, sherry,* and *madeira.* They are wines with added alcohol. (Natural wine never contains more than about 17 per cent. of alcohol.)
Gin, like whisky, but flavoured with juniper.	

48. The alcohol of commerce ("spirits of wine") always contains water. To obtain anhydrous or *absolute* alcohol from this, lumps of quicklime are added to spirit containing a high percentage of alcohol, until the quicklime shows itself above the surface of the liquid. The latter is allowed to stand for some days, or boiled for several hours under a reflux-condenser (18), and then distilled. The preparation is much facilitated, and the loss, rather large by this method, reduced to a minimum, by heating a spirit of high percentage with a small quantity of quicklime in a vat, closed by a screwed-down cover, for some hours at 100° in a water-bath. The spirit is then distilled. To prepare absolute alcohol from dilute alcohol, the latter must first be concentrated by distillation from a water-bath. The dehydration can also be effected by addition of solid potassium carbonate, which causes the liquid to separate into two layers,

the aqueous one below and the alcoholic one above. Alcohol of 91·5 per cent. by weight is thus obtained.

Absolute alcohol is a mobile, colourless liquid of characteristic odour. It solidifies at $-112{\cdot}3°$, and burns with a pale-blue, non-luminous flame. It is very hygroscopic, being miscible with water in all proportions with contraction and rise in temperature. The maximum contraction is obtained by mixing 52 volumes of alcohol with 48 volumes of water, the volume of the resulting mixture at 20° being 96·3 instead of 100.

The presence of water in alcohol can be detected by anhydrous copper sulphate, which remains perfectly colourless when in contact with absolute alcohol, whereas if the slightest trace of water is present, the copper sulphate develops a light-blue colour after several hours. The specific gravity, a physical constant often employed to ascertain the purity of liquid compounds, can also be employed for the same purpose.

A simple and rapid method for the estimation of alcohol in mixtures with water is very necessary for industrial and fiscal purposes, and a practical method, due to VON BAUMHAUER, MENDELÉEFF, and others, consists in the determination of the specific gravity and temperature of such a mixture. A table has been prepared with great accuracy, showing the specific gravities of mixtures of alcohol and water from 0 to 100 per cent., at temperatures between 0° and 30°. When the specific gravity and temperature of a given mixture have been determined, the percentage of alcohol may be found by reference to the table. In practice the specific gravity is usually determined with a delicate hydrometer.

In commerce and in the arts, the amount of alcohol is usually expressed on the Continent of Europe in *volume-percentage*, or the number of litres of absolute alcohol contained in 100 litres of the aqueous solution. In Great Britain the standard is *proof-spirit.* This name is derived from the old method of testing spirit by moistening gunpowder with it, and then bringing the mixture into contact with a lighted match. If the alcohol were "under proof," the powder did not take fire, but if there were sufficient alcohol present, the application of the light ignited the gunpowder, the spirit being then "over proof." When the proportions of alcohol and water were such that it was just possible to set fire to the powder, the sample was described as "proof-spirit." When the spirit is weaker than proof-spirit it is said to be *under proof*, and when stronger than proof-spirit is said to be *over proof;* for example, a spirit 5° under proof would contain in each 100 volumes the same quantity of alcohol as 95 volumes of proof-spirit, and a spirit 5° over proof would need 5 volumes of water added to each 100 volumes to convert it into proof-spirit. By act of Parliament "proof-spirit" is defined as "such a spirit as shall at a temperature of 51° F. weigh exactly $\frac{12}{13}$ of an equal measure of distilled water." This corresponds to a spirit containing 57·1 per cent. of alcohol by volume, or 49·3 per cent. by weight.

For scientific purposes the amount of alcohol is usually expressed in percentage by weight, or the number of grammes of alcohol contained in 100 grammes of the aqueous solution. These percentage-numbers are not the same, the percentages by weight being smaller than those by volume for a spirit of any given concentration.

The greater part of the alcohol produced is consumed in the form of beverages, their detrimental physiological effects being augmented by the impurities, especially fusel-oil, which they contain. Alcohol is used in commerce for the preparation of lacquers, varnishes, dyes, important pharmaceutical preparations such as chloroform, chloral, iodoform, and others, and as a motive power for motor-vehicles. It is also employed for the preservation of anatomical specimens. Alcohol is a good solvent for many organic compounds, and finds wide application in laboratory-work for this purpose.

On account of the extensive use of alcohol for manufacturing processes, some industries would be paralyzed if the necessary spirit were subject to the same excise-duty as alcohol intended for consumption. The alcohol used in manufactures in some countries is accordingly made unfit for drinking (*denatured* or *methylated*) by the addition of materials which impart to it a nauseous taste, and is sold duty-free. On the Continent of Europe crude wood-spirit is employed for this purpose, and in Great Britain this is supplemented by the addition of a small quantity of paraffin-oil. The sale of denatured alcohol is also permitted in the United States.

In the United States the tax on alcohol is $1.10 per proof gallon (50 per cent. alcohol by volume), or $2.07 per standard gallon

(231 cubic inches of 94 per cent. alcohol by volume). The duty is much higher in Great Britain, being 14*s.* 9*d.* per gallon of proof-spirit (British standard, p. 57). Besides permitting the sale of methylated spirit containing naphtha, the British Government allows the sale for manufacturers' use of alcohol denatured with wood-spirit only, under the name "Industrial spirit." It has the important advantage of being wholly miscible with water. In the chemical laboratories of universities and colleges in Great Britain and Ireland, the use of duty-free pure alcohol is permitted.

A test for ethyl alcohol is the formation of iodoform on the addition of iodine and caustic potash (152).

Propyl Alcohols, $C_3H_7 \cdot OH$.

49. Two *propyl alcohols* are known, one boiling at 97° and having a specific gravity of 0·804, the other boiling at 81° and having a specific gravity of 0·789. In accordance with the principles which have been stated, only two isomerides are possible:

$$\underset{\text{Normal propyl alcohol}}{CH_3 \cdot CH_2 \cdot CH_2OH}, \quad \text{and} \quad \underset{\textit{iso}\text{Propyl alcohol}}{CH_3 \cdot CH(OH) \cdot CH_3}.$$

The structure to be assigned to the substance with the higher boiling-point, and that to the substance with the lower, may be determined by submitting the substances to oxidation. From each of these alcohols is thus obtained a compound with the formula C_3H_6O, but these oxidation-products are not identical. On further oxidation, the compound C_3H_6O (propionaldehyde), obtained from the alcohol of higher boiling-point, yields an acid $C_3H_6O_2$, called propionic acid; whereas the substance C_3H_6O (acetone), formed from the alcohol of lower boiling-point, is converted into carbon dioxide and acetic acid, $C_2H_4O_2$:

$$C_3H_8O \text{ (propyl alcohol, B.P. 97°)} \rightarrow C_3H_6O \text{ (propionaldehyde)} \rightarrow$$
$$\rightarrow C_3H_6O_2 \text{ (propionic acid)};$$

$$C_3H_8O \text{ (\textit{iso}propyl alcohol, B.P. 81°)} \rightarrow C_3H_6O \text{ (acetone)} \rightarrow$$
$$\rightarrow CO_2 + C_2H_4O_2 \text{ (acetic acid)}.$$

Propionic acid has the constitution $CH_3 \cdot CH_2 \cdot COOH$, and acetone $CH_3 \cdot CO \cdot CH_3$, as will be shown later. It will be observed that only the normal alcohol is capable of forming propionic acid, because the production of this substance must be due to the replacement of two hydrogen atoms by one oxygen atom, and with the normal alcohol this can only yield a compound with the structure assigned to propionic acid. On the other hand, the formation of a substance with the constitution of acetone by removal of two hydrogen atoms from a compound C_3H_8O is only possible when the latter has the structure of *iso*propyl alcohol. The alcohol of higher boiling-point must therefore be *n*-propyl alcohol, and that boiling at the lower temperature must be *iso*propyl alcohol.

Oxidation affords a general method for distinguishing primary from secondary alcohols. By referring to the formulæ given in 44, it is seen that all primary alcohols contain the group $-\mathrm{CH_2OH}$, which is converted by oxidation into the carboxyl-group $-\mathrm{C}{\leqslant}^{\mathrm{O}}_{\mathrm{OH}}$, the characteristic group of organic acids. Further, all secondary alcohols contain the group $\mathrm{H\cdot\overset{|}{\underset{|}{C}}\cdot OH}$: removal of the two hydrogen atoms from this yields the group $\mathrm{\overset{|}{\underset{|}{C}}{:}O}$, characteristic of the *ketones* (119), the homologues of acetone. *The oxidation of a primary alcohol and that of a secondary alcohol produce respectively an acid and a ketone with the same number of carbon atoms as the original alcohol.*

A further induction may be made from these reactions. In the conversion of normal propyl alcohol into propionic acid, as well as of *iso*propyl alcohol into acetone, the oxidation occurs at the carbon atom already linked to oxygen. This is always so, and the general rule may be stated as follows: *when an organic compound is submitted to oxidation, the molecule is attacked at the part which already contains oxygen—that is, where oxidation has already begun.*

Normal propyl alcohol is obtained by fractionation of fusel-oil, and is a colourless liquid of agreeable odour. It is miscible with water in all proportions. *iso*Propyl alcohol is also a liquid: it is *not* present in fusel-oil, but can be obtained by the reduction of acetone (120 and 156).

Butyl Alcohols, $C_4H_9\cdot OH$.

50. Four *butyl alcohols* are known (*cf.* Table, **44**), which is the number possible according to the theory, and it is necessary to consider whether these theoretically possible formulæ are in accord with the properties of the four isomerides. On oxidation, the two alcohols boiling at 117° and 107° respectively yield acids with the same number of carbon atoms. They must therefore have the structures 1 and 3 (*Ibid.*), since each contains the group —CH_2OH. For reasons referred to later, the alcohol boiling at 117° is considered to have the normal structure (1), and that boiling at 107° the structure (3). A third butyl alcohol, boiling at 100°, is converted by oxidation into a ketone with the same number of carbon atoms, showing that it must be a secondary alcohol corresponding with structure (2). Lastly, for the fourth, which is solid at ordinary temperatures, melting at 25·5° and boiling at 83°, since three of the theoretically possible structural formulæ have been assigned to the other isomerides, there remains only the fourth structure, that of a tertiary alcohol. This structure for the alcohol melting at 25·5°, thus arrived at by elimination, is in accordance with its chemical behaviour. On oxidation, for example, it yields neither an acid nor a ketone with four carbon atoms, but the molecule is at once decomposed into substances containing a smaller number of carbon atoms. Since to yield on oxidation an acid with the same number of carbon atoms, an alcohol must contain the group —CH_2OH, and to produce a ketone with the same number of carbon atoms, it must contain the group $H\cdot\overset{|}{\underset{|}{C}}\cdot OH$, it is evident that neither of these can be obtained from a tertiary alcohol. If the oxidation takes place in this, as in every other case, at the carbon atom already linked to oxygen, it must result in the decomposition of the molecule.

The foregoing holds for tertiary alcohols in general, so that oxidation affords a means of distinguishing between primary, secondary, and tertiary alcohols. The experimental proof can be summed up as follows.

A primary alcohol yields on oxidation an acid with the same number of carbon atoms: a secondary alcohol yields on oxidation a *ketone with the same number of carbon atoms: whereas oxidation of a tertiary alcohol at once decomposes the molecule, yielding compounds with a smaller number of carbon atoms.*

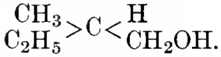
Many other methods of ascertaining whether an alcohol is primary, secondary, or tertiary are available, one of the simplest being based on the effects of heat. Primary alcohols are stable at 360°, the boiling-point of mercury. At this temperature, secondary alcohols decompose, yielding chiefly hydrocarbons of the series C_nH_{2n} (**122**) and water; but they are stable at 218°, the boiling-point of naphthalene. At the last temperature tertiary alcohols are decomposed, yielding similar products to those formed from secondary alcohols at 360°. In practice, the constitution of any alcohol is ascertainable by determining its vapour-density at both these temperatures with VICTOR MEYER's apparatus (**11**), the decision being based on the normal or abnormal character of the results obtained.

Amyl Alcohols, $C_5H_{11}\cdot OH$.

51. The alcohols containing five carbon atoms are called *amyl alcohols*. There are eight possible isomerides, and all are known (*cf.* Table, **44**). They are liquids with a disagreeable odour, like that of fusel-oil. *iso*Butylcarbinol, $(CH_3)_2CH\cdot CH_2\cdot CH_2OH$, and secondary butylcarbinol, $CH_3\cdot CH(C_2H_5)\cdot CH_2OH$, are the principal constituents of fusel-oil (**47**).

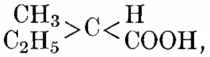
Secondary butylcarbinol furnishes a very remarkable example of isomerism. It is shown in **37** how the arrangement of the atoms in a molecule accounts for the phenomenon of isomerism. A careful study of the properties of a compound makes it possible to assign to it a structural formula, to the exclusion of all the other formulæ possible for its known molecular composition. On the other hand, any given structural formula represents only *one* compound, since such a formula is the expression of a very definite set of properties: when they are unlike for two compounds, the difference must be indicated by their structural formulæ.

Nevertheless, there are three isomeric amyl alcohols which have been shown by careful examination to have the same structural formula:



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\CH_2OH.\end{matrix}$$

That they have this constitution is proved by the fact that on oxidation they yield valeric acid with the structure



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\COOH,\end{matrix}$$

as can easily be proved by synthesis (166).

The three amyl alcohols with this constitution have identical chemical properties and nearly all their physical constants are the same. One of the latter, however, serves to distinguish them from one another. When a beam of plane-polarized light is passed through layers of these alcohols, the plane of polarization is rotated by one isomeride to the left, and by another to the right, while the third alcohol produces no rotation. The first two are said to be *optically active* (27, 2).

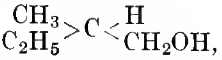
Since the difference between optically active compounds depends only upon a physical property, while their chemical properties are identical, it may be asked whether this difference is not a purely *physical* one, arising from differences in the arrangement of the *molecules*, such as is supposed to exist in dimorphous substances. The objection to this view is twofold.

First, differences in the arrangement of the molecules can only be supposed to exist in the case of *solid* substances, because it is only in them that the molecules have a fixed position in relation to one another. It is assumed that the molecules of liquids and gases are free to move; but they, too, afford examples of optical activity. For liquids there is still a possibility that not the molecules themselves, but conglomerations of them arranged in a definite manner may be free to move. Were this the cause of optical activity, on conversion into gases of normal vapour-density, optically active liquids should produce no rotation in the plane of polarization. That they actually do produce this rotation was proved by BIOT, and later by GERNEZ. This phenomenon cannot be attributed to a difference in the arrangement of the molecules, because in a vapour of normal density each molecule is capable of independent motion.

Second, the optical activity is displayed in derivatives of optically active substances.

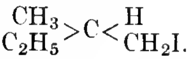
Hence it follows that *an explanation of the rotation of the plane of polarization by liquids and dissolved substances must be sought for in the internal structure of the molecules.*

It is now necessary to determine what peculiarity in the structure of the molecules causes this phenomenon. The following considerations will furnish an insight into this. The *lævo-rototory amyl alcohol*, with the constitution



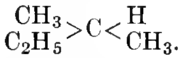
$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\CH_2OH,\end{matrix}$$

is converted by the action of gaseous hydriodic acid into *amyl iodide*, with the structural formula



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\CH_2I.\end{matrix}$$

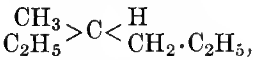
This compound is *optically active.* On treatment with nascent hydrogen, the iodine atom is replaced by hydrogen, with formation of *pentane*,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\CH_3.\end{matrix}$$

This compound is *optically inactive.*

If amyl iodide is subjected to the action of ethyl iodide in the presence of sodium, there results a *heptane*,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}H\\CH_2\cdot C_2H_5,\end{matrix}$$

and this substance is *optically active.*

An examination of these three optically active substances shows that they differ from optically inactive pentane in the respect that, of the four groups linked to the central carbon atom, in the latter two (methyl) are similar, whereas in the others they are all different.

52. VAN 'T HOFF has shown that *most optically active compounds contain at least one carbon atom linked to four different atoms or groups; and he has designated a carbon atom so linked an* asymmetric *carbon atom.*

As stated above, there are three amyl alcohols with the same constitutional formula, of which one is dextro-rotatory, the second lævo-rotatory, and the third optically inactive. Three such isomerides always exist when there is one asymmetric carbon atom in the molecule, and of the two optically active substances one causes exactly the same amount of dextro-rotation as the other of lævo-rotation. Van 't Hoff has shown that the existence of this number of isomerides is a necessary consequence of the presence of one asymmetric carbon atom in a molecule, provided certain assumptions are made regarding the relative positions of the atoms in space. These assumptions are as follows.

The quadrivalency of the carbon atom has its origin in four points of attraction, situated on its outer surface, so that it is able to link itself to atoms or groups of atoms in four directions. The only supposition about these directions in agreement with the facts is that *the carbon atom is situated at the centre of a regular four-sided figure* (*tetrahedron*) *with its linkings directed toward the angles* (Fig. 24). By putting the groups R, P, and Q of compounds CR_2Q_2, CR_2PQ, or CR_3P in different positions in two atom models,* it is always possible by rotating the models to bring them into such a position that the like groups coincide, showing that the two forms are identical. Such compounds do not exhibit optical isomerism.

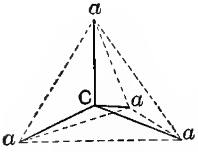


Fig. 24.—Carbon Tetrahedron.

For compounds C·RPQS, containing four different groups and therefore an asymmetric carbon atom, the possibility of the existence of two isomeric forms is indicated. It

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* The comprehension of what follows will be considerably facilitated by the construction of several models of carbon atoms with their linkings. This is easily done by cutting out a sphere from a cork to represent the carbon atom, the linkings being represented by moderately thick wires about ten centimetres long, with ends filed to a point. These wires are fixed in the cork sphere in the manner shown in Fig. 24. To show the linking of the atoms or groups of atoms, cork spheres of different colours are fastened to the ends of the wires, the different colours indicating dissimilar groups.

is seen from Figs. 25 and 26 (and still better from models) that for these four groups two arrangements are possible, which cannot be made to coincide in any position, although they resemble one another as an object resembles its reflection in a mirror. Such a figure has no plane of symmetry, hence the name "asymmetric carbon atom."

53. It is thus possible to understand how one isomeride causes as much dextro-rotation as the other lævo-rotation (**52**), for the arrangement of the groups relative to the asymmetric carbon atom must be the cause of the rotation of the plane of polarization. If the arrangement of the groups in Fig. 25 produces dextro-rotation, then the inverse arrangement in the isomeride in Fig. 26 must necessarily cause an equal rotation, but in an opposite direction.

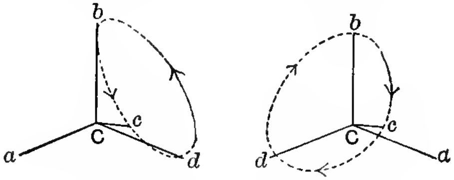

FIG. 25. FIG. 26.

ASYMMETRIC C-ATOMS.

It was stated above that not merely two, but three, isomerides are possible when there is one asymmetric carbon atom present in the molecule; a dextro-rotatory, a lævo-rotatory, and an optically inactive isomeride. It has been proved that the optically inactive substance is composed of equal parts of the dextro-rotatory and of the lævo-rotatory compound. Since these rotations are equal in amount, but different in direction, their sum has no effect upon the plane of polarization.

This isomerism in space, called *stereochemical isomerism* or *stereoisomerism*, is not indicated in the ordinary structural formulæ written in one plane: hence the apparent contradiction that a single structural formula may represent two different compounds. VAN 'T HOFF's theory, however, supports the fundamental principle that all isomerism has its origin in a difference in the arrangement of the atoms in the molecule.

In addition to the explanation of optical isomerism just given, two others might be suggested, although both can be shown to be untenable. Thus, the four linkings of the carbon atom might be supposed unequal in value; so that such a compound as CP_3Q could exist in isomeric forms. Experience contradicts this assumption.

This phenomenon might also be supposed to be due to a difference in the motion of the atoms in the molecule. Then isomerism could no longer exist at absolute zero, since atomic motion ceases at this point; and a falling temperature should cause a marked diminution in the difference between the optical isomerides. There is, however, not the slightest indication of such behaviour.

Higher Alcohols, $C_nH_{2n+1}\cdot OH$.

54. The properties of the *higher alcohols* are mentioned in **45.** Here may be cited *cetyl alcohol,* $C_{16}H_{33}\cdot OH$, obtained from spermaceti, and *myricyl alcohol,* $C_{30}H_{61}\cdot OH$, obtained from wax. The number of isomerides of these higher compounds possible is very great, while the number actually known is but small. Of the higher members of the series, only the normal primary compounds are known.

Alkoxides.

55. *Alkoxides* (alcoholates) are compounds obtained from alcohols by exchange of the hydroxyl-hydrogen atom for metals (**43**). The best known are *sodium methoxide* (methylate), $CH_3\cdot ONa$, and *sodium ethoxide* (ethylate), $C_2H_5\cdot ONa$. Both are white powders, and yield crystalline compounds with the corresponding alcohol. They dissolve readily in the alcohols, and, as will be seen later, are constantly used in syntheses. It was formerly supposed that the addition of water to a solution of an alkoxide converted it completely into an alkali-metal hydroxide, and liberated an equivalent quantity of alcohol; but LOBRY DE BRUYN has shown this to be only partly true, an equilibrium being reached in the reaction:

$$C_2H_5ONa + H_2O \rightleftarrows C_2H_5OH + NaOH.$$

A proof of this is given in **61.** It follows that a solution of sodium hydroxide in alcohol is partly decomposed into water and sodium alkoxide.

The alcoholic solution of sodium ethoxide, usually obtained by dissolving pieces of sodium in absolute ethyl alcohol, gradually becomes brown in consequence of oxidation to aldehyde (115). On the other hand, the solution of sodium methoxide in methyl alcohol remains unaltered, and therefore is employed in syntheses more than that of sodium ethoxide.

ALKYL HALIDES, ESTERS, AND ETHERS.

56. Many compounds containing a hydroxyl-group are known in inorganic chemistry: they are called bases, and display a close resemblance in properties. This similarity may be attributed to their common possession of the group OH, which is present in their aqueous solutions as an ion.

An aqueous solution of alcohol does not conduct an electric current, so that the alcohol is not ionized. This is supported by the fact that such a solution is not alkaline, and therefore contains no OH-ions.

Notwithstanding this fact, the alcohols possess a basic character in so far that, like bases, they combine with acids with elimination of water:

$$\underset{\text{Alcohol}}{M\cdot\boxed{OH}}\boxed{+\underset{\text{Acid}}{H}}\cdot R=\underset{\text{Ester}}{M\cdot R}+HOH.$$

The substances formed are comparable with the salts of inorganic chemistry, and are called *compound ethers* or *esters*. The different natures of bases and of alcohols are displayed, however, in the mode of formation of their salts, which is quite unlike that in which esters are produced. A salt is formed from an acid and base instantaneously: it is a reaction of the ions, because the hydrogen ion of the acid unites with the hydroxyl ion of the base ("Inorganic Chemistry," 66):

$$\underset{\text{Base}}{[\dot{B}+OH']}+\underset{\text{Acid}}{[\dot{H}+Z']}=\underset{\text{Salt}}{[\dot{B}+Z']}+H_2O.$$

The formation of esters, on the other hand, takes place very slowly, especially at ordinary temperatures, the reaction being between the non-ionized alcohol and the acid:

$$\underset{\text{Alcohol}}{R\cdot OH}+\underset{\text{Acid}}{[\dot{H}+Z']}=\underset{\text{Ester}}{R\cdot Z}+H_2O.$$

Reactions between ions usually take place instantaneously, those between molecules slowly.

Many bases can lose water, with formation of anhydrides or oxides: alcohols behave similarly. By the abstraction of one molecule of water from two molecules of an alcohol, compounds called *ethers* with the general formula $C_nH_{2n+1}—O—C_nH_{2n+1}$ are formed. By elimination of water from two different alcohols, compounds called *mixed ethers* with the general formula

$$C_nH_{2n+1}—O—C_mH_{2m+1}$$

are produced.

Alkyl Halides.

57. The alkyl halides may be regarded as the hydrogen-halide esters of the alcohols, as their formation from alcohol and a hydrogen halide shows:

$$C_nH_{2n+1}\boxed{OH+H}X = C_nH_{2n+1}X+H_2O.$$

In preparing alkyl halides by this method, the alcohol is first saturated with the dry hydrogen halide, and then heated in a sealed tube or under a reflux-condenser. The reaction may also be carried out by heating the alcohol with sulphuric acid and sodium or potassium halide:

$$C_2H_5OH+H_2SO_4+KBr = C_2H_5Br+KHSO_4+H_2O.$$

Two other methods of formation for alkyl halides are mentioned in **30** and **43**: they are more fully treated below.

Action of Phosphorus Halides on Alcohols.—These sometimes react together very energetically. In preparing alkyl bromides and iodides, it is usual to employ phosphorus with bromine or iodine instead of the bromide or iodide of phosphorus itself. For example, in the preparation of ethyl bromide, red phosphorus is added to strong alcohol, in which it is insoluble. Bromine is then added drop by drop, the temperature of the liquid being kept from rising by a cooling agent. Each drop of bromine unites with phosphorus to form phosphorus tribromide, and it reacts with the alcohol, producing ethyl bromide:

$$PBr_3+3C_2H_5OH = PO_3H_3+3C_2H_5Br.$$

The careful addition of bromine is continued until a quantity corresponding to that required by the equation has been used. The mixture is then allowed to stand for some time, so that the reaction may be as complete as possible, the final product consisting *chiefly* of phosphorous acid and ethyl bromide. Since the latter boils at 38·4°, and the acid is not volatile, it is possible to separate them by distillation, which can be effected by immersing the flask containing the mixture in a water-bath heated above the temperature mentioned.

58. *Action of Halogens on Hydrocarbons.*—Only chlorides and bromides can be prepared thus, because iodine does not react with hydrocarbons. The method is seldom used for the preparation of alkyl halides, since, from two causes, mixtures of alkyl halides are obtained which are sometimes very difficult to separate: whereas, by employing other methods, these compounds are produced without admixture of similar substances.

One of these causes is that whenever one molecule of a hydrocarbon C_nH_{2n+2} is brought into contact with one molecule of chlorine or bromine, the reaction does not take place merely as indicated by the equation

$$C_nH_{2n+2}+Cl_2 = C_nH_{2n+1}Cl+HCl,$$

but that compounds $C_nH_{2n}Cl_2$, $C_nH_{2n-1}Cl_3$, etc., are simultaneously formed, a portion of the hydrocarbon remaining unacted on.

It is possible to avoid the formation of these higher substitution-products by bringing the halogens into contact with the *vapour* of the boiling hydrocarbons.

The other cause is that the halogen replaces hydrogen in different positions in the molecule. Thus, chlorine reacts with normal pentane to form simultaneously primary and secondary amyl chlorides,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl \quad \text{and} \quad CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3,$$

as can be proved by converting these chlorides into the corresponding alcohols and oxidizing the latter (49).

59. The following table gives some of the physical properties of the alkyl halides.

Alkyl-group.	Name.	Chloride.		Bromide.		Iodide.	
		Boiling-point.	Specific Gravity.	Boiling-point.	Specific Gravity.	Boiling-point.	Specific Gravity.
CH_3	Methyl	−23·7°	0·952(0°)	4·5°	1·732(0°)	45°	2·293(18°)
C_2H_5	Ethyl	12·2°	0·918(8°)	38·4°	1·468(13°)	72·3°	1·944(14°)
C_3H_7	*n*-Propyl	46·5°	0·912(0°)	71°	1·383(0°)	102·5°	1·786(0°)
C_4H_9	*n*-Prim. butyl	78°	0·907(0°)	101°	1·305(0°)	130°	1·643(0°)
C_5H_{11}	*n*-Prim. amyl	107°	0·901(0°)	129°	1·246(0°)	156°	1·543(0°)

It will be noticed that only the lower chlorides and methyl bromide are gaseous at the ordinary temperature, most of the others being liquids, and the highest members solids. The specific gravities of all the chlorides are less than 1, and diminish as the number of carbon atoms increases. The specific gravities of the lower bromides and iodides are considerably greater than 1, although they also diminish with increase in the number of carbon atoms, so that the highest members of the homologous series are specifically lighter than water. All are very slightly soluble in water, but dissolve readily in many organic solvents. The lower members have a pleasant ethereal odour.

Chemical Properties.—In their action upon silver nitrate the alkyl halides differ very much from the halides of the metals. In aqueous or alcoholic solution the latter at once yield a precipitate of silver halide, the reaction being quantitative. On the other hand, silver nitrate either does not precipitate silver halide from a solution of the alkyl halides, or the reaction only takes place slowly. The explanation is the same as that given in 56, that in the first case the action is one between ions, and in the second between molecules. This proves that there are either no halogen ions present in an alkyl halide solution, or at least that their number is very small.

The alkyl halides can be converted into one another; for example, alkyl iodides can be obtained by heating the corresponding chlorides with potassium or calcium iodide. These reactions are often incomplete.

The alkyl iodides are chiefly used for introducing alkyl-groups into organic compounds.

Alkyl fluorides are also known, and are more volatile than the corresponding chlorides. They are obtained by the action of silver fluoride on an alkyl iodide, and in other ways.

Esters of Other Mineral Acids.

60. Esters of a great number of mineral acids are known. The general methods for their preparation are as follows.

1. By the action of the acid on absolute alcohol:

$$\underset{\text{Alcohol}}{C_2H_5\cdot}\boxed{OH+H}\underset{\text{Nitric acid}}{\cdot ONO_2} = H_2O+\underset{\text{Ethyl nitrate}}{C_2H_5\cdot ONO_2}.$$

2. By the action of an alkyl halide on a silver salt:

$$SO_4\boxed{Ag_2+2I}C_2H_5 = \underset{\text{Ethyl sulphate}}{SO_4(C_2H_5)_2}+2AgI.$$

3. By the action of mineral-acid chlorides on alcohols or alkoxides:

$$\underset{\text{Phosphorus oxychloride}}{PO}\boxed{Cl_3+3Na}OC_2H_5 = \underset{\text{Normal ethyl phosphate}}{PO(OC_2H_5)_3}+3NaCl.$$

The acid esters of sulphuric acid, called *alkylsulphuric acids,* are of some importance. *Ethylsulphuric acid,* or *ethyl hydrogen sulphate,* $C_2H_5O\cdot SO_2\cdot OH$, is obtained by mixing alcohol with concentrated sulphuric acid. The formation of this compound is never quantitative, because an equilibrium is reached in the reaction (99). The alkylsulphuric acids are separated from the excess of sulphuric acid by means of their barium (or strontium or calcium) salts, these compounds being readily soluble in water, while the sulphates are insoluble, or nearly so. It is only necessary to neutralize the mixture of sulphuric acid and alkylsulphuric acid with barium carbonate, the product being a solution of barium ethylsulphate, $\genfrac{}{}{0pt}{}{ba^*}{C_2H_5}{>}SO_4$. The free ethylsulphuric acid is then obtained by the addition of the calculated quantity of sulphuric acid to this solution. At ordinary temperatures it is an odourless, oily, strongly acid liquid, miscible with water in all proportions. The aqueous solution decomposes into sulphuric acid and

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* ba $= \frac{1}{3}$Ba.

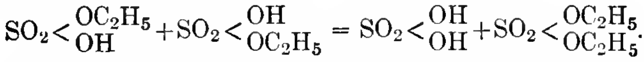
alcohol, slowly at the ordinary temperature, but quickly at the boiling-point.

The barium salts of the amylsulphuric acids, obtained from the amyl alcohols and sulphuric acid, have different solubilities in water, and Pasteur effected their partial separation by fractional crystallization. By this means he was able to separate approximately the optically active amyl alcohol from *iso*butylcarbinol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH$. Both are present in the mixture of amyl alcohols boiling at 131°–132° obtained by the fractional distillation of fusel-oil. *iso*Butylcarbinol is the chief constituent of the mixture of amyl alcohols boiling at this temperature.

Ethylsulphuric acid forms well-crystallized salts. Its potassium salt is used in the preparation of ethyl compounds; for example, ethyl bromide is readily prepared by the dry distillation of a mixture of potassium bromide and potassium ethylsulphate:

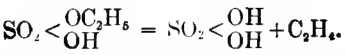
$$\underset{\text{Potassium ethylsulphate}}{KO\cdot SO_2\cdot O\cdot\boxed{C_2H_5+Br}K} = \underset{\text{Potassium sulphate}}{KO\cdot SO_2\cdot OK}+\underset{\text{Ethyl bromide}}{C_2H_5Br}.$$

When free ethylsulphuric acid is heated, the neutral ethyl ester of sulphuric acid and free sulphuric acid are formed:



$$SO_2<\begin{matrix}OC_2H_5\\OH\end{matrix}+SO_2<\begin{matrix}OH\\OC_2H_5\end{matrix}=SO_2<\begin{matrix}OH\\OH\end{matrix}+SO_2<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}.$$

Simultaneously, free sulphuric acid and ethylene are produced (125):



$$SO_2<\begin{matrix}OC_2H_5\\OH\end{matrix}=SO_2<\begin{matrix}OH\\OH\end{matrix}+C_2H_4.$$

The conversion of ethylsulphuric acid into ether is described in 62.

Dimethyl sulphate, $(CH_3)SO_4$, is obtained by the vacuum-distillation of methylsulphuric acid:

$$2CH_3HSO_4=(CH_3)_2SO_4+H_2SO_4.$$

It is an oily liquid, boiling at 188°, and is often employed in the introduction of methyl-groups into organic compounds.

Ethers.

61. The *ethers* are isomeric with the alcohols. Their constitution is proved by WILLIAMSON's synthesis, the action of an alkoxide on an alkyl halide:

$$C_nH_{2n+1}\cdot O\cdot \boxed{Na+I}\cdot C_mH_{2m+1} = C_nH_{2n+1}\cdot O\cdot C_mH_{2m+1} + NaI.$$

This synthesis affords confirmation of the constitution of the alkoxides indicated in 43, that the metal occupies the place of the hydroxyl-hydrogen. For, supposing it were otherwise, the metal having replaced a hydrogen atom directly linked to carbon, then sodium methoxide, for example, would have the formula $Na\cdot CH_2\cdot OH$. On treatment with ethyl iodide, this compound would yield propyl alcohol:

$$C_2H_5\cdot \boxed{I+Na}\cdot CH_2OH = C_2H_5\cdot CH_2OH + NaI.$$

This reaction does not take place. Methylethyl ether, with the empirical formula of an alcohol, but none of its properties, is produced instead.

> WILLIAMSON's synthesis is also possible when the alkoxide is dissolved in dilute alcohol (50 per cent.). Though so much water is present, the reaction is almost quantitative. It follows that the greater part of the sodium alkoxide must be present as such, and is therefore not decomposed by the water into alcohol and sodium hydroxide (55), because then the formation of the ether would necessarily be prevented.

62. The best-known compound of the homologous series of ethers is *diethyl ether*, $C_2H_5\cdot O\cdot C_2H_5$, usually called "ether." This compound is manufactured, and also prepared in the laboratory, from sulphuric acid and ethyl alcohol. For this purpose a mixture of five parts of alcohol (90 per cent.) is heated with nine parts of concentrated sulphuric acid at 130°–140°. When ether and water begin to distil, alcohol is allowed to flow into the distillation-flask to keep the volume of liquid constant. Ether passes over continuously, but after about six times as much alcohol has been added as was in the first instance mixed with the sulphuric acid, the distillate becomes richer and richer in alcohol, and finally the formation of ether stops altogether. Methylated spirit may be substituted for pure spirit, the product being called "methylated ether."

The explanation of this process is as follows. The alcohol and sulphuric acid first form ethylsulphuric acid (60). Ethylsulphuric acid is decomposed by heating with water, the acid and alcohol being regenerated:

$$C_2H_5\cdot\boxed{OSO_3H+H}OH = C_2H_5\cdot OH+H_2SO_4.$$

When, however, ethyl alcohol instead of water reacts with ethylsulphuric acid, ether and sulphuric acid are formed in an exactly analogous manner:

$$C_2H_5\cdot\boxed{O\cdot SO_3H+H}\cdot O\cdot C_2H_5 = C_2H_5\cdot O\cdot C_2H_5+H_2SO_4.$$

The production of ether depends upon the formation of ethylsulphuric acid, and subsequent decomposition of this compound into ethyl ether and sulphuric acid by the addition of more alcohol. Since the sulphuric acid is regenerated in this reaction, it yields a fresh quantity of ethylsulphuric acid, so that the process is continuous. This would lead to the expectation that a small quantity of sulphuric acid could convert an unlimited amount of alcohol into ether, but this is not borne out by experience. The explanation is that in the formation of ethylsulphuric acid from alcohol and sulphuric acid, water is formed as a by-product:

$$C_2H_5\cdot\boxed{OH+H}SO_4H = C_2H_5\cdot SO_4H+H_2O.$$

This water partly distils along with the ether, but partly remains in the flask, decomposing the ethylsulphuric acid as formed into alcohol and sulphuric acid. When the amount of water in the reaction-mixture exceeds a certain limit, it prevents the formation of ethylsulphuric acid altogether, thus putting an end to the production of ether.

When another alcohol is allowed to flow into the original mixture instead of ethyl alcohol, shortly before the distillation begins, a mixed ether is obtained:

$$C_2H_5\cdot\boxed{SO_4H+H}\cdot O\cdot C_5H_{11} = C_2H_5\cdot O\cdot C_5H_{11}+H_2SO_4.$$

This reaction proves that the formation of ether takes place in the two stages mentioned above.

The crude ether thus obtained contains water, alcohol, and small quantities of sulphur dioxide. It is left in contact with quicklime for several days, the water, sulphur dioxide, and part of the alcohol being thus removed. It is then distilled from a water-bath heated to about 55°. To remove the small quantity of alcohol remaining, it is extracted several times with small volumes of water, and the water run off. The ether is separated from dissolved water by distillation, first over calcium chloride and finally over sodium.

63. Diethyl ether is a colourless, very mobile liquid of agreeable odour, boiling at 35·4°, and solidifying at −117·6°. Prolonged breathing of it produces unconsciousness, followed by but slightly disagreeable consequences on awakening. Ether is therefore used in surgery as an anæsthetic. It is slightly soluble in water, one volume dissolving in 11·1 volumes of water at 25°: on the other hand, water dissolves slightly in ether (2 per cent. by volume at 12°). On account of its low boiling-point, ether is very volatile, and as its vapour is highly combustible, burning with a luminous flame, and producing an explosive mixture with air, it is a substance requiring very careful handling. Intense cold is produced by its evaporation, the outside of a flask containing it becoming coated with ice when the evaporation of the ether is promoted by the introduction of a rapid stream of air.

In the laboratory, ether is an invaluable solvent and crystallizing-medium for many compounds, and is used for extracting aqueous solutions (24). It is also of great utility in many manufacturing processes.

Homologues.

64. The ethers are comparatively stable towards chemical reagents. Dilute acids, alkalis, and phosphorus pentachloride have no action on them at the ordinary temperature. Sodium is unable to displace any of their hydrogen. When, however, they are treated with hydrogen halides, halogen compounds are formed. Thus, gaseous hydriodic acid passed into an ether at the ordinary temperature produces an alcohol and an alkyl iodide:

$$C_nH_{2n+1}\cdot\boxed{O\cdot C_mH_{2m+1}+H}\cdot I = C_nH_{2n+1}\cdot I+C_mH_{2m+1}\cdot OH.$$

At higher temperatures water and an alkyl iodide are formed:

$$C_nH_{2n+}\cdot\boxed{O}\cdot C_mH_{2m+1}+\boxed{2H}\cdot I = C_nH_{2n+1}\cdot I + C_mH_{2m+1}\cdot I + H_2O.$$

Isomerism.—This may be caused, as in the alcohols, by branching of the carbon chains, by the alteration of the position of the oxygen atom in the molecule, or by both causes simultaneously.

ALKYL-RADICALS LINKED TO SULPHUR.

65. The elements grouped in the same column of the periodic system ("Inorganic Chemistry," 211–221) yield similar compounds, a fact traceable to their having equal valencies: they also have similar chemical properties. Experience has shown that organic compounds containing elements of such a group display the properties of their inorganic analogues in every variety of similarity and dissimilarity, their points of resemblance and of difference being sometimes even more marked than those of the inorganic compounds. A comparison of the oxygen compounds treated of up to this point with the sulphur compounds of similar structure will serve as an example.

The alcohols and ethers may be regarded as derived from water by the replacement of one or both of its hydrogen atoms by alkyl. The corresponding sulphur compounds are similarly derived from sulphuretted hydrogen, and are represented thus:

$$C_nH_{2n+1}\cdot SH \quad \text{and} \quad C_nH_{2n+1}\cdot S\cdot C_mH_{2m+1}.$$

The first are called *mercaptans*, and the second *thioethers.*

The resemblance of these compounds to the alcohols and ethers is chiefly noticeable in their methods of formation, for if potassium hydrogen sulphide instead of potassium hydroxide reacts with an alkyl halide, a mercaptan is formed:

$$C_nH_{2n+1}\cdot\boxed{X+K}\cdot SH = C_nH_{2n+1}\cdot SH + KX.$$

Like the alcohols, the mercaptans have one, and only one, hydrogen atom in the molecule replaceable by metals. It is therefore reasonable to suppose that the hydrogen atom thus distinguished from all the others is linked to sulphur, the other hydrogen atoms being linked to carbon.

Just as the ethers are formed by the action of alkyl halides on alkoxides, so the thioethers are obtained by treating the metallic compounds of the mercaptans, the *mercaptides*, with alkyl halides:

$$C_nH_{2n+1}\cdot S\cdot \boxed{Na+I}\cdot C_mH_{2m+1} = C_nH_{2n+1}\cdot S\cdot C_mH_{2m+1} + NaI.$$

Water is a neutral compound, and sulphuretted hydrogen is a weak acid; in consequence alcohol does not form alkoxides with the bases of the heavy metals, whereas mercaptans yield mercaptides with them. An alcohol soluble with difficulty in water, such as amyl alcohol, does not dissolve in alkalis; but the mercaptans, although insoluble in water, dissolve readily in alkalis, forming mercaptides. They therefore possess an acidic character.

Mercaptans.

66. The mercaptans can also be obtained by the action of phosphorus pentasulphide upon alcohols:

$$5C_nH_{2n+1}\cdot OH + P_2S_5 \rightarrow 5C_nH_{2n+1}\cdot SH;$$

or by distilling a solution of potassium alkylsulphate with potassium hydrogen sulphide:

$$C_2H_5\cdot \boxed{O\cdot SO_3K+K\cdot}SH = C_2H_5\cdot SH + K_2SO_4.$$

They are liquids almost insoluble in water, with boiling-points markedly lower than those of the corresponding alcohols. Thus, *methyl mercaptan* boils at 6°, methyl alcohol at 66°. They are characterized by their *exceedingly disagreeable odour*, a property characteristic of almost all volatile sulphur compounds. Our olfactory organs are very sensitive to mercaptans, and can detect the merest traces of them, even when quite unrecognizable by chemical means.

Many metallic compounds of the mercaptans are known, some of them in well-crystallized forms. The *mercury mercaptides* furnish an example of these bodies, and are produced by the action of mercaptans on mercuric oxide, whence the name of these compounds is derived (by shortening *corpus mercurio aptum* to *mercaptan*). Many of the other heavy metals, such as lead, copper, and bismuth, yield mercaptides: the lead compounds have a yellow colour. The mercaptan is liberated from all mercaptides by the addition of mineral acids.

Thioethers.

67. In addition to the methods given in 65 for the preparation of thioethers, the action of potassium sulphide, K_2S, upon the salts of alkylsulphuric acids may be employed:

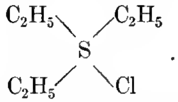
$$\underset{\substack{\text{Potassium}\\\text{ethylsulphate}}}{2C_2H_5\boxed{O\cdot SO_3K+K_2}S} = (C_2H_5)_2S+2K_2SO_4.$$

The thioethers are neutral compounds with an exceedingly offensive odour. They are liquids insoluble in water, and yield double compounds with metallic salts, such as $(C_2H_5)_2S\cdot HgCl_2$.

With one molecule of an alkyl iodide the thioethers form remarkable crystalline compounds of the type $(C_2H_5)_3SI$. These compounds, called *sulphonium iodides*, are readily soluble in water. Moist silver oxide replaces the I-atom by hydroxyl:

$$(C_2H_5)_3SI+AgOH = (C_2H_5)_3SOH+AgI.$$

The *sulphonium hydroxides* thus obtained dissolve easily in water, and are very alkaline in reaction. They are strong bases, absorbing carbon dioxide from the air, and yielding salts with acids. In the *sulphonium halides*, such as $(C_2H_5)_3S\cdot Cl$, sulphur is the only element to which the univalent alkyl-groups and univalent Cl-atom can be united, so that these substances must have constitutional formulæ of the type



The mercaptans resemble sulphuretted hydrogen in being slowly oxidized by contact with air, whereby they are converted into disulphides like *diethyl disulphide*,

$$C_2H_5\cdot S\cdot S\cdot C_2H_5.$$

The hydrogen linked to sulphur has been removed by oxidation, so that the disulphides have the constitution given above. A further proof is their formation when potassium ethylsulphate is heated with potassium disulphide, K_2S_2.

Numerous inorganic compounds containing oxygen and sulphur exist. Similar substances are also known in organic chemistry.

The *sulphoxides*, $\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}>SO$, are formed by the oxidation of thioethers with nitric acid. Their constitution is indicated by the fact that they are very easily reduced to thioethers. If the oxygen were linked to carbon, they would not behave in this manner, because neither alcohols nor ethers lose their oxygen by gentle reduction.

The *sulphones* are compounds with the constitution $\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}>SO_2$, as shown in 68. They are formed by energetic oxidation of the thioethers, and also by oxidizing sulphoxides. Nascent hydrogen is unable to effect their reduction.

Sulphonic Acids.

68. The *sulphonic acids* result when mercaptans undergo vigorous oxidation (with nitric acid). They have the formula $C_nH_{2n+1}\cdot SO_3H$. During this oxidation the alkyl-group remains intact, for the salts of these sulphonic acids are also formed by interaction of an alkyl iodide and a sulphite:

$$C_2H_5\boxed{I+K}SO_3K = KI + C_2H_5SO_3K.$$

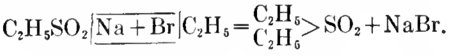
Since the sulphur in mercaptans is directly linked to carbon, the same is true of the sulphonic acids. This is further proved by the fact that on reduction the latter yield mercaptans. The structure of ethylsulphonic acid is therefore $CH_3\cdot CH_2\cdot SO_3H$.

The group SO_3H must contain a hydroxyl-group, because PCl_5 yields with a sulphonic acid a *sulphonyl chloride*, $C_nH_{2n+1}\cdot SO_2Cl$, from which the sulphonic acld may be regenerated by the action of water. The structure of the compound is therefore

$$CH_3\cdot CH_2\cdot SO_2\cdot OH.$$

The alkylsulphonic acids are strongly acidic, very hygroscopic, crystalline substances, and are very soluble in water.

In the sulphonyl chlorides, chlorine can be replaced by hydrogen in the nascent state. The bodies thus obtained have the formula $C_nH_{2n+1}\cdot SO_2H$, and are called *sulphinic acids*. When an alkyl halide reacts with the sodium salt of a sulphinic acid, a sulphone (67) is formed:



$$C_2H_5SO_2\boxed{Na+Br}C_2H_5 = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}>SO_2 + NaBr.$$

This mode of preparation is a proof of the constitution of the sulphones.

Selenium and *tellurium* compounds corresponding to most of these sulphur compounds are known, and have also a most offensive odour.

ALKYL-RADICALS LINKED TO NITROGEN.

I. AMINES.

69. At the beginning of the last chapter (65) it was stated that the properties possessed by inorganic compounds are even more marked in their organic derivatives. The compounds to be described in this chapter afford another striking example of this phenomenon.

The term *amines* is applied to substances which may be regarded as derived from ammonia by exchange of hydrogen for alkyl-radicals. The most characteristic property of ammonia is its power of combining with acids to form salts by direct addition:

$$NH_3 + H \cdot X = NH_4 \cdot X.$$

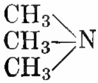
Tervalent nitrogen is thereby made quinquivalent, a change apparently intimately connected with its basic character. This property is also found among the alkylamines. They are, at least those low in the series, better conductors of electricity for the same molecular concentration of their aqueous solutions, and are therefore more strongly basic than ammonia itself ("Inorganic Chemistry," 66 and 238). This applies also to the organic compounds corresponding to ammonium hydroxide, NH_4OH. The last-named substance is not known in the free state, but it exists in the aqueous solution of ammonia. It is very unstable, being completely decomposed into water and ammonia by boiling its solution. It has only weakly basic properties, because there are but few NH_4-ions and OH-ions in its aqueous solution, apparently because the compound NH_4OH has a very strong tendency to break up into NH_3 and H_2O. Such a decomposition is, however, no longer possible for compounds containing four alkyl-groups in place of the four hydrogen atoms of the NH_4-group, and experience has shown that these compounds possess great stability. Since the nitrogen cannot revert to the tervalent condition, their basic character, in comparison with that of NH_4OH, is so strengthened that they are ionized to the same degree as the alkalis, being almost completely dissociated in $\frac{1}{10}$-normal solutions.

The amines yield complex salts fully analogous to the platinum salt, $(NH_4)_2PtCl_6$, and the gold salt, NH_4AuCl_4, of ammonia.

Nomenclature and Isomerism.

70. The amines are called *primary, secondary,* or *tertiary,* according to whether one, two, or three hydrogen atoms of NH_3 have been exchanged for alkyl-radicals. The compounds NR_4OH, in which R stands for an alkyl-radical, are called *quaternary ammonium bases.*

Isomerism of the amines may be due to different causes. First, to branching of the carbon chain, just as in the alcohols and other compounds. Second, to the position occupied by the nitrogen in the molecule. Third, to both causes simultaneously. In addition to these, the primary, secondary, and tertiary nature of the amines must be taken into account. A compound C_3H_9N, for example, can be propylamine or *iso*propylamine, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ or $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH{\cdot}NH_2$, primary; methylethylamine, $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}NH$, secondary; or trimethylamine,



$$\begin{matrix}CH_3\diagdown \\ CH_3{-}N \\ CH_3\diagup\end{matrix}$$

tertiary.

Methods of Formation.

71. HOFMANN discovered that when an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, the following reactions take place.

$$\text{I. } C_nH_{2n+1}{\cdot}Cl + pNH_3 = HCl + C_nH_{2n+1}NH_2 + (p-1)NH_3.$$

The alkyl-group thus takes the place of one hydrogen atom in NH_3, this atom uniting with the halogen atom of the alkyl halide to form a hydrogen halide. This acid can unite with the primary amine formed, or with the ammonia, and in fact combines with a portion of each.

The primary amine remaining free reacts further with the alkyl halide in the same way:

$$\text{II. } C_nH_{2n+1}Cl + qNH_2\cdot C_nH_{2n+1} = HCl + (C_nH_{2n+1})_2NH + \\ + (q-1)NH_2\cdot C_nH_{2n+1}.$$

A part of this secondary amine also remains free and enters into reaction in its turn:

$$\text{III. } C_nH_{2n+1}\cdot Cl + r(C_nH_{2n+1})_2NH = HCl + (C_nH_{2n+1})_3N + \\ + (r-1)NH(C_nH_{2n+1})_2.$$

Lastly, the tertiary amine, which also remains partly free, unites with the alkyl halide, yielding the halide of a quaternary ammonium base:

$$\text{IV. } (C_nH_{2n+1})_3N + C_nH_{2n+1}\cdot Cl = (C_nH_{2n+1})_4N\cdot Cl.$$

It is assumed that excess of ammonia is employed; but even when it is otherwise, and in general for every proportion of alkyl halide and ammonia, the reaction takes place in these four phases. The final result is, therefore, that the primary, secondary, and tertiary amines, and the ammonium base, are formed together. It is often possible, however, so to adjust the proportion of ammonia and alkyl halide, together with the duration of the reaction, etc., that a given amine is the main product, and the quantities of the other amines are small. The nature of the alkyl-group also exercises a great influence upon the character of the reaction-product.

The separation of the ammonium bases from the ammonia and amines is simple, because, while the amines are liquids volatilizing without decomposition, or gases, the ammonium bases are not volatile. When, therefore, the mixture of the amine hydrohalides and the ammonium bases is distilled after addition of caustic potash, only the free amines pass over.

To separate the primary amines from the mixture of the hydrohalides of the three amines, fractional crystallization is often employed for the lower members, methylamine, dimethylamine, and so on. The propylamines and those succeeding can be separated by fractional distillation.

Various methods of preparing primary amines unmixed with secondary or tertiary are known (**85**, **104**, **264**, **274**, and **371**).

The *velocity of the formation of tetraalkylammonium iodides* from triethylamine and an alkyl iodide or bromide has been investigated by MENSCHUTKIN. It is apparently a bimolecular reaction ("Inorganic Chemistry," **50**), and therefore takes place according to the equation

$$s = \frac{dx}{dt} = k(a-x)(b-x),$$

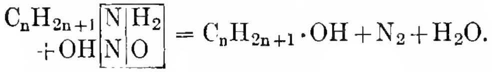
where s is the velocity, k the constant of the reaction, a and b the quantities of amine and iodide per unit volume expressed in molecules, and x the quantity of both which has entered into reaction after the time t. For the investigation of these velocities, weighed quantities of the amine and iodide are brought into contact in a suitable solvent, the solution heated in a sealed tube at 100°, and after known intervals of time x determined. With the aid of higher mathematics it is possible to solve the equation for k, and it is found that the value of k is constant for every reaction: that is, if corresponding sets of values are substituted for t and x in the equation, on solving it the same value is always obtained for k. The greater the molecular weight of the alkyl-radical, the smaller is k, although the decrease is not very marked: for example, when the amine reacts with propyl bromide, $k=0{\cdot}00165$; with octyl bromide $k=0{\cdot}00110$ (with acetone as solvent). The equation is always applicable, being independent of the solvent used, as might be expected from the fact that it does not contain any term dependent upon the nature of the solvent. There was made, however, an unexpected observation of the extraordinarily great influence exercised by the nature of the solvent upon the values of k. Using hexane as a solvent, $k=0{\cdot}000180$ for the combination of triethylamine and ethyl iodide: for methyl alcohol, on the other hand, $k=0{\cdot}0516$, or 286·6 times as great.

In many other instances the nature of the solvent exercises an important influence upon the velocity of reaction, but a satisfactory explanation of the phenomenon is still lacking.

Properties.

72. The primary, secondary, and tertiary amines are sharply distinguished from one another by their different behaviour towards nitrous acid, $HO\cdot NO$.

Primary amines yield alcohols, with evolution of nitrogen:



$$\begin{array}{r|c|c|}\cline{2-3} C_nH_{2n+1} & N & H_2 \\ +OH & N & O \\ \cline{2-3}\end{array} = C_nH_{2n+1}\cdot OH + N_2 + H_2O.$$

The reaction is fully analogous to the decomposition of ammonium nitrite into water and nitrogen:

$$NH_3\cdot HONO = \begin{array}{|c|c|c|}\hline H\cdot & N & H_2 \\ HO & N & O \\ \hline\end{array} = 2H_2O + N_2.$$

Secondary amines yield *nitrosoamines:*

$$(C_nH_{2n+1})_2N\boxed{H+HO}NO = (C_nH_{2n+1})_2N\cdot NO + H_2O.$$

The lower members are yellowish liquids of characteristic odour, and are slightly soluble in water. They are easily reconverted into secondary amines by the action of concentrated hydrochloric acid (315): this is a proof of the structure given above, because if the nitroso-group were directly linked to a carbon atom either by its oxygen or by its nitrogen, it would not be possible thus to reconvert the nitrosoamine into a secondary amine.

Tertiary amines are either unacted on, or oxidized, by nitrous acid.

Their behaviour with nitrous acid therefore affords a means of distinguishing the three classes of amines from one another. It also serves as a basis for the separation of the secondary and tertiary amines in the pure state from a mixture of the two. When a concentrated solution of sodium nitrite is added to a hydrochloric-acid solution of a mixture of the two amines, the secondary amine is converted into a nitrosoamine: this collects as an oil on the surface of the aqueous solution, and can be removed by means of a separating-funnel. The tertiary amine is not attacked, but remains in the aqueous solution in the form of a salt: it can be obtained by distilling with caustic potash. Any primary amine present is decomposed during the process.

Another method of distinguishing between primary, secondary, and tertiary amines consists in the determination of the number of alkyl-groups with which the amine can combine. For example, if a compound C_3H_9N is propylamine, $C_3H_7NH_2$, it should yield, when heated with excess of methyl iodide, a compound

$$\begin{matrix}C_3H_7\\(CH_3)_3\end{matrix}NI = C_6H_{16}NI:$$

or if $C_3H_9N = \begin{matrix}C_2H_5\\CH_3\end{matrix}>NH$, the same treatment should yield $\begin{matrix}C_2H_5\\(CH_3)_3\end{matrix}NI = C_5H_{14}NI$: or lastly, if $C_3H_9N = (CH_3)_3N$, there would be obtained $(CH_3)_4NI = C_4H_{12}NI$. A titration of the iodine ion of the quaternary ammonium iodide formed determines whether C_3H_9N is primary, secondary, or tertiary.

HOFMANN's test for primary amines is described in **84**.

Individual Members.

73. The lower members are inflammable gases, and are very soluble in water; thus, 1150 volumes of methylamine dissolve in one volume of water at 12·5°. The succeeding members have low boiling-points, and are miscible with water in all proportions. Both they and the lower members have a characteristic ammoniacal odour, like boiled lobsters. The higher members are odourless and insoluble in water. The specific gravities of the amines are considerably less than 1, that of methylamine being only 0·699 at −11°. The following table indicates the variations of their boiling-points.

Alkyl-Radical.	Primary.	Secondary.	Tertiary.
Methyl	−6°	7°	3·5°
Ethyl	19°	56°	90°
n-Propyl	49°	98°	156°
n-Butyl	76°	160°	215°
n-Octyl	180°	297°	366°

Methylamine occurs in *Mercurialis perennis*: it is readily prepared by the interaction of ammonia and dimethyl sulphate. *Dimethylamine* (**316**) and *trimethylamine* are constituents of herring-brine.

Trimethylamine, $(CH_3)_3N$, can be readily prepared by heating ammonium chloride with formaldehyde ("Formalin," 117) in an autoclave at 120°–160°:

$$2NH_3 + 9CH_2O = 2(CH_3)_3N + 3CO_2 + 3H_2O.$$

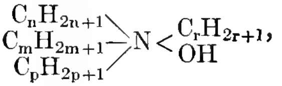
Tetramethylammonium hydroxide, $(CH_3)_4N \cdot OH$, is obtained by treating a solution of the corresponding chloride in methyl alcohol with the equivalent quantity of caustic potash. After filtering off the precipitated potassium chloride, the solution is diluted with water, and evaporated *in vacuo* at 35° to remove the alcohol. The base crystallizes out as hydrates, which are very hygroscopic and absorb carbon dioxide readily. It is decomposed by heat into trimethylamine and methyl alcohol:

$$(CH_3)_4N \cdot OH = (CH_3)_3N + CH_3OH.$$

The higher ammonium bases are converted by dry distillation into a tertiary amine, water, and a hydrocarbon C_nH_{2n}:

$$(C_2H_5)_4N \cdot OH = \underset{\text{Triethylamine}}{(C_2H_5)_3N} + \underset{\text{Ethylene}}{C_2H_4} + H_2O.$$

The structure of the ammonium bases is thus explained. Only the nitrogen atom is able to link to itself the four univalent alkyl-groups and the univalent hydroxyl-group. It must be assumed to be quinquivalent in these compounds, and the constitution of the ammonium bases is therefore



$$\left.\begin{matrix} C_nH_{2n+1} \\ C_mH_{2m+1} \\ C_pH_{2p+1} \end{matrix}\right\rangle N < \begin{matrix} C_rH_{2r+1} \\ OH \end{matrix},$$

n, m, p, and r being similar or dissimilar.

Alkyl-derivatives of *hydrazine* or *diamide*, $H_2N \cdot NH_2$, are also known. Among the methods for their preparation may be mentioned the direct introduction of an alkyl-group into hydrazine, and the careful reduction of nitrosoamines (72). They have little power of resisting oxidizing agents, reducing an alkaline copper solution, for example, at the ordinary temperature.

74. *Triethylamine* is soluble in water, although at about 20° this solution separates into two layers. The upper consists of a solution of water in the amine, and the lower of a solution of the amine

in water. In the neighbourhood of 20° a slight rise in temperature effects this separation into two layers, merely holding the tube for a short time in the warm hand being sufficient.

This separation at a definite temperature is best understood from a consideration of the solubility-curve of the system *amine + water.* This amine (Fig. 27) is less soluble in warm water than in

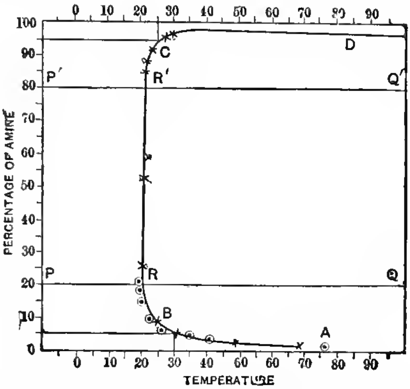


FIG. 27.—SOLUBILITY-CURVES FOR TRIETHYLAMINE AND WATER.

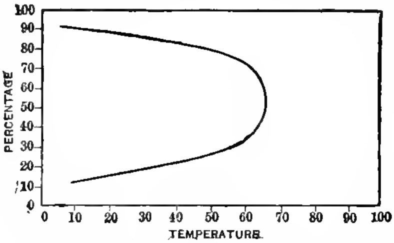


FIG. 28.—USUAL FORM OF SOLUBILITY-CURVE FOR TWO LIQUIDS.

cold, and below 20° is miscible with water in all proportions. If, for example, increasing quantities of the amine be added to water at 30°, it dissolves until the amount of amine reaches about 5 per cent. (*cf.* Fig. 27). The solution is then saturated, and addition of more of the amine produces a second layer of liquid. On the other hand, when water is added to triethylamine at 25°, it dissolves until the amount of water reaches about 5 per cent. (*cf.* Fig. 27). Beyond this point two layers are formed. The line *DC* is the solubility-curve for water dissolved in triethylamine, and the line *AB* that for triethylamine in water. When the temperature falls, on the one hand the solubility of the water in the amine increases, and on the other that of the amine in the water, so that the solubility-curves meet between *B* and *C*. The whole area is divided into two parts by the solubility-curves. All points within *ABCD* correspond with two layers of liquid, and all points outside it with a homogeneous mixture.

If, for example, the abscissa *PQ* is drawn for a mixture of 20 per cent. of amine and 80 per cent. of water, the mixture is homogeneous for all temperatures up to the point *R*, and heterogeneous above that temperature. Along the very steep portion of the curve, represented in this special case by the part *BC*, a slight rise in temperature must evidently result in separation of the liquid; because although at about 20° (the point *R*) an 80 per cent. amine solution of water and a 20 per cent. aqueous solution of amine are just about to form, at *R'* (less than 1° higher) the separation would produce an 80 per cent. aqueous solution of amine and a 20 per cent. amine solution of water. It follows that in this part of the curve a small rise of temperature must cause a separation of water sufficient to alter the composition of one of the layers from 20 per cent. to 80 per cent. of amine.

It has been already mentioned that the relative solubility-curve for the system *water + triethylamine* has an abnormal path in the portion *BC*. Moreover, the whole curve differs from those ordinarily obtained. The solubility of liquids partially miscible with one another usually increases with the temperature, just as in the case of solids and liquids, so that the ordinary curve is therefore the converse of that in Fig. 27, and is usually as represented in Fig. 28.

II. NITRO-COMPOUNDS.

75. When silver nitrite reacts with an alkyl iodide, two compounds are formed, both with the empirical formula $C_nH_{2n+1}NO_2$, but having different boiling-points. From ethyl iodide, for example, a substance $C_2H_5NO_2$, boiling at 17°, and another boiling at 113°-114°, are obtained. The two isomerides are therefore readily separated by fractionation.

The compound of lower boiling-point is decomposed into alcohol and nitrous acid by the action of caustic potash. It must therefore be looked upon as an ester of nitrous acid, being formed thus:

$$C_nH_{2n+1}\boxed{I+Ag}\cdot ONO = C_nH_{2n+1}\cdot ONO + AgI.$$

When these esters, or *alkyl nitrites*, are reduced, they are converted into an alcohol and ammonia.

The compound boiling at the higher temperature behaves quite differently. It is not converted into a nitrite and alcohol by the action of alkalis, and on reduction its two oxygen atoms are replaced by two hydrogen atoms, with formation of a primary amine:

$$C_nH_{2n+1}NO_2 \rightarrow C_nH_{2n+1}NH_2.$$

The last reaction shows that the nitrogen in this class of compounds is directly linked to carbon, because it is so in the amines. The oxygen atoms can be linked only to the nitrogen, because the reduction to amine takes place at the ordinary temperature. Under these conditions it is not possible to replace oxygen directly linked to carbon, for neither alcohols nor ethers are reduced at low temperatures to substances not containing oxygen. This leads to the conclusion that these substances, called *nitro-compounds*, have the constitution $C_nH_{2n+1}—NO_2$.

Nitro-compounds therefore contain a group NO_2, the nitrogen atom being directly linked to carbon; this group is called the nitro-group.

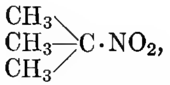
The names of these compounds are formed from those of the saturated hydrocarbons by means of the prefix *nitro*. The compound CH_3NO_2 is thus *nitromethane;* $C_2H_5NO_2$ is *nitroethane;* and so on. The members of this homologous series are called *nitro-paraffins*. They are colourless liquids of ethereal odour: the lower members are slightly soluble in water. They all distil without decomposition.

76. The nitro-derivatives have a number of characteristic properties, among them the possession of one hydrogen atom replaceable by alkali-metals, especially sodium. This sodium compound is most readily obtained by the action of sodium ethoxide or methoxide upon the nitro-compound in absolute-alcoholic solution. A fine, white, crystalline precipitate is thus formed, that from nitroethane, for example, having the composition $C_2H_4NaNO_2$. The insolubility of these sodium compounds in absolute alcohol is sometimes employed in the separation of the nitroparaffins from other substances.

This power of exchanging hydrogen for sodium only exists when at least one hydrogen atom is linked to the carbon atom carrying the nitro-group. As from nitroethane, a metallic compound is obtained from secondary nitropropane,

$$CH_3{\cdot}CH{<}^{CH_3}_{NO_2};$$

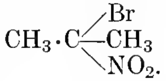
but tertiary nitrobutane,



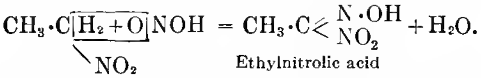
$$(CH_3)_3 \equiv C\cdot NO_2,$$

does *not* yield any corresponding metallic derivative. The structure of these metallic compounds is considered in **311**.

When an alkaline solution of a nitro-compound is brought into contact with bromine, one (or more) of its hydrogen atoms linked to the same carbon atom as the nitro-group is replaced by bromine. This reaction is analogous to the substitution by metals, it being still possible, for example, to introduce one bromine atom into $CH_3\cdot CHBrNO_2$, but not into $CH_3\cdot C{\begin{smallmatrix}Br\\CH_3\\NO_2\end{smallmatrix}}$.



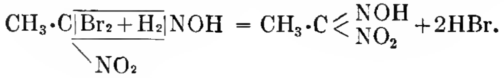
77. The behaviour of nitro-compounds with nitrous acid is very characteristic, and affords a method of distinguishing between primary, secondary, and tertiary nitro-derivatives. The reaction is carried out by adding sodium nitrite to an alkaline solution of the nitro-compound, and acidifying with dilute sulphuric acid. From a primary nitro-compound, an *alkylnitrolic acid* is formed:



$$CH_3\cdot C\boxed{H_2+O}NOH \atop \diagdown NO_2 = CH_3\cdot C{<}{N\cdot OH \atop NO_2} + H_2O.$$

Ethylnitrolic acid

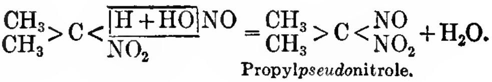
The constitution of these compounds is indicated by their production from a dibromonitro-compound by the action of hydroxylamine, H_2NOH:



$$CH_3\cdot C\boxed{Br_2+H_2}NOH \atop \diagdown NO_2 = CH_3\cdot C{<}{NOH \atop NO_2} + 2HBr.$$

The alkylnitrolic acids dissolve in alkalis, yielding metallic compounds of blood-red colour, this reaction affording a characteristic test for them. They crystallize well, but are by no means stable.

When similarly treated, the secondary nitro-compounds yield pseudo*nitroles*. They contain the group $=C{<}{NO \atop NO_2}$:



$${CH_3 \atop CH_3}{>}C{<}{\boxed{H+HO}NO \atop NO_2} = {CH_3 \atop CH_3}{>}C{<}{NO \atop NO_2} + H_2O.$$

Propyl*pseudo*nitrole.

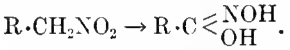
When solid, the *pseudo*nitroles are colourless, crystalline substances, but have an intense blue colour in the fused state or in solution. This characteristic serves as a test for them.

Lastly, the tertiary nitro-compounds are not acted on by nitrous acid.

Among the other properties of nitro-compounds is their decomposition into the acid with the same number of carbon atoms and hydroxylamine, by heating with hydrochloric acid:

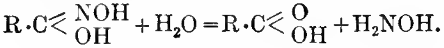
$$\underset{\text{Nitroethane}}{CH_3{\cdot}CH_2{\cdot}NO_2} + H_2O = \underset{\text{Acetic acid}}{CH_3{\cdot}COOH} + \underset{\text{Hydroxylamine}}{H_2NOH}.$$

The mechanism of this reaction is explicable on the assumption that the nitro-compound is first transformed into a *hydroxamic acid*:



$$R{\cdot}CH_2NO_2 \rightarrow \underset{\text{Hydroxamic acid}}{R{\cdot}C{<}^{NOH}_{OH}}.$$

The hydroxamic acid is then converted by the water present into the acid and hydroxylamine:



$$R{\cdot}C{<}^{NOH}_{OH} + H_2O = \underset{\text{Acid}}{R{\cdot}C{<}^{O}_{OH}} + \underset{\text{Hydroxylamine}}{H_2NOH}.$$

ALKYL-RADICALS LINKED TO OTHER ELEMENTS.

I. ALKYL-RADICALS LINKED TO ELEMENTS OF THE NITROGEN GROUP.

78. Ammonia unites readily with acids, with formation of salts. Phosphine, PH_3, also possesses this property, although the phosphonium salts, PH_4X, are decomposed even by water into an acid and phosphine.

The basic character has wholly disappeared in arsine, AsH_3, and stibine, SbH_3. Bismuth does not yield a hydride, and possesses only very slight traces of the characteristics of metalloids.

Ammonia cannot be easily oxidized, and is unacted on by the oxygen of the atmosphere at ordinary temperatures. On the other hand, the hydrides of phosphorus, arsenic, and antimony are readily oxidized.

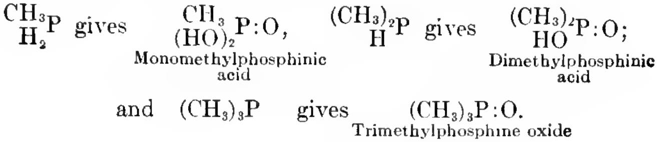
All these properties are displayed by the compounds of these elements with alkyl-radicals.

Phosphines.

79. The amines yield stronger bases than ammonia. Similarly, the *phosphines* form stronger bases than phosphine. In both cases this property becomes more marked as the number of alkyl-groups replacing hydrogen atoms increases. The salts of the monoalkylphosphines, for example, are decomposed by water, whereas those of the dialkylphosphines and trialkylphosphines are not. The *quaternary phosphonium bases*, PR_4OH, are as strongly basic as the ammonium bases. When a phosphonium base is heated, it does not, like an ammonium base (73), decompose into an alcohol (or $C_nH_{2n} + H_2O$) and a trialkyl base, but into a hydrocarbon C_nH_{2n+2} and an oxygen compound:

$$(C_2H_5)_4P \cdot OH = C_2H_6 + (C_2H_5)_3PO.$$

This substance is called *triethylphosphine oxide*. In this reaction the great affinity between phosphorus and oxygen plays an important part. This affinity is also indicated by the ease with which the phosphines undergo oxidation, a change effected even by the action of the air. Nitric acid oxidizes phosphine, PH_3, to phosphoric acid, $OP(OH)_3$: in an analogous manner the phosphines take up one oxygen atom, and in addition as many oxygen atoms as there are hydrogen atoms directly linked to phosphorus:



$$\begin{matrix}CH_3\\H_2\end{matrix}P \text{ gives } \begin{matrix}CH_3\\(HO)_2\end{matrix}P{:}O, \qquad \begin{matrix}(CH_3)_2\\H\end{matrix}P \text{ gives } \begin{matrix}(CH_3)_2\\HO\end{matrix}P{:}O;$$

Monomethylphosphinic acid

Dimethylphosphinic acid

$$\text{and } (CH_3)_3P \text{ gives } (CH_3)_3P{:}O.$$

Trimethylphosphine oxide

The constitution of these compounds is established by a variety of considerations: for instance, by the fact that the *monoalkylphosphinic acids* are dibasic, that the *dialkylphosphinic acids* are monobasic, and that the *trialkylphosphine oxides* have no acidic properties.

The phosphines are colourless liquids of penetrating, stupefying odour. Methylphosphine, CH_3PH_2, is a gas: in very small quantities triethylphosphine has an odour of hyacinths.

Methods of Formation.—Only tertiary phosphines and phosphonium compounds are formed by the action of alkyl halides upon phosphine, PH_3. Primary and secondary phosphines are obtained by heating phosphonium iodide, PH_4I, with an alkyl iodide and zinc oxide.

Arsines.

80. The *primary* and *secondary arsines*, H_2AsCH_3 and $HAs(CH_3)_2$, are obtained by reduction of monomethylarsinic acid and dimethylarsinic acid, $(CH_3)HAsO \cdot OH$ and $(CH_3)_2AsO \cdot OH$, by amalgamated zinc-dust and hydrochloric acid. Both are immediately oxidized by the air. *Tertiary arsines* do not yield bases with water. They are formed by the action of a zinc alkide on arsenic chloride, $AsCl_3$, and from sodium arsenide and an alkyl iodide:

$$AsNa_3 + 3C_2H_5I = As(C_2H_5)_3 + 3NaI.$$

Quaternary arsonium bases, however, have strongly marked basic properties. They are prepared by the addition of alkyl halides to tertiary arsines, and treatment of the resulting halide with silver hydroxide.

The best-known arsenic derivatives containing alkyl-radicals are the *cacodyl compounds*. They were investigated by BUNSEN, who gave them this name in consequence of their offensive smell. They are very poisonous. The name *cacodyl* is applied to the univalent group $\begin{matrix}CH_3\\CH_3\end{matrix}\!>As—$. *Cacodyl oxide*, $[(CH_3)_2As]_2O$, is formed by distilling arsenious oxide with the acetate of an alkali-metal. All the other cacodyl compounds are obtained from cacodyl oxide; thus, *cacodyl chloride*, $(CH_3)_2AsCl$, is prepared by heating the oxide with hydrochloric acid, and *cacodyl*, $(CH_3)_2As\cdot As(CH_3)_2$, by heating the chloride with zinc in an atmosphere of carbon dioxide. When brought into contact with air, both ignite spontaneously.

Stibines and Bismuthines.

The *tertiary stibines* and the *quaternary stibonium bases* have been obtained from antimony. The first-named are very readily oxidized, taking fire spontaneously in the air. The stibonium bases are as basic in character as the corresponding nitrogen, phosphorus, and arsenic derivatives. The *pentamethyl-derivative* $Sb(CH_3)_5$ is also known.

Bismuth does not yield a hydride, but *tertiary bismuthines*, such as $(C_2H_5)_3Bi$, have been prepared. They are very unstable, and explode when heated. They do not form addition-products with alkyl halides, so that the "bismuthonium" bases are unknown.

II. ALKYL-RADICALS LINKED TO THE ELEMENTS OF THE CARBON GROUP.

81. The elements in each group or column of the periodic system are divided into two sub-groups: in one the elements are electro-positive and base-forming; in the other electro-negative and acid-forming ("Inorganic Chemistry," 213). In the first division of the carbon group are titanium, zirconium, and thorium; in the second, carbon, silicon, germanium, tin, and lead. *Only elements belonging to electro-negative sub-groups are capable of yielding alkyl-compounds*, this being true not only of the carbon group of elements, but also of the elements of the other groups. In 1870, MENDELÉEFF for this reason predicted that the then unknown element germanium would, in accordance with its position in the periodic system, yield alkyl-derivatives; this prediction was confirmed by the researches of WINKLER, to whom science is indebted for the discovery of this

element. Titanium belongs to the electro-positive sub-group, and though in many respects it resembles silicon, it has not been possible to prepare its alkyl-derivatives.

Like carbon, the elements silicon, germanium, tin, and lead are quadrivalent. Numerous attempts have been made to prepare compounds containing chains of silicon atoms resembling the carbon chains. They have not been successful, no compounds containing a chain of more than three silicon atoms having been prepared. As far, therefore, as is at present known, silicon lacks the power of forming long chains like those present in many carbon compounds. On account of this defect, a "Chemistry of Silicon," analogous to the "Chemistry of Carbon," is not possible.

The silicon alkides have a character analogous to that of the similarly constituted alkyl-derivatives of carbon. For example, *silicon tetraethide*, $Si(C_2H_5)_4$, and *tetraethylmethane*, $C(C_2H_5)_4$, are known. Both are liquids, and are not acted upon by either fuming nitric acid or fuming sulphuric acid at ordinary temperatures, but yield substitution-products with chlorine. *Silicoheptane*, $(C_2H_5)_3SiH$, has a petroleum-like odour, a resemblance to *triethylmethane*, $(C_2H_5)_3CH$.

Organic compounds of tin containing a tin atom linked to four dissimilar groups, and therefore possessing an *asymmetric tin atom*, have been prepared by POPE. He has also succeeded in resolving these derivatives into their optically active components, and KIPPING has effected the resolution of *asymmetric silicon compounds*, proofs that optical activity does not depend on the nature of the carbon atom, but is inherent in every asymmetric arrangement of groups round a central atom.

III. METALLIC ALKIDES.

82. When excess of ethyl iodide is warmed with zinc, a white crystalline compound, C_2H_5ZnI, is formed, and on stronger heating it yields *zinc ethide*, $Zn(C_2H_5)_2$, and zinc iodide:

$$2C_2H_5ZnI = Zn(C_2H_5)_2 + ZnI_2.$$

Zinc ethide can be separated by distillation, which must be performed in an apparatus filled with an inert gas, because this compound, like the other zinc alkides, burns spontaneously when exposed to air.

The metallic alkides are colourless liquids, heavier than water. Zinc methide boils at 46°, zinc ethide at 118°, and zinc propide at 146°.

When an alkyl iodide reacts with a zinc alkide, a saturated hydrocarbon is formed:

$$\begin{matrix}CH_3\\CH_3\end{matrix}>\boxed{Zn+\begin{matrix}I\\I\end{matrix}}\begin{matrix}\cdot CH_3\\\cdot CH_3\end{matrix}=ZnI_2+2CH_3\cdot CH_3.$$

Water converts zinc alkides into saturated hydrocarbons and zinc oxide:

$$Zn(CH_3)_2+H_2O=2CH_4+ZnO.$$

The halogens react very energetically with zinc alkides, yielding alkyl halides.

Sodium alkides and *potassium alkides* are formed by the action of sodium and potassium respectively upon zinc alkides. These metals dissolve in zinc alkides, precipitating an equivalent quantity of zinc. Sodium alkides and potassium alkides have not been obtained in the pure state, but only in solution in zinc alkides.

Very remarkable compounds of magnesium have been obtained by GRIGNARD. When magnesium-turnings are brought into contact with a dry ethereal solution of an alkyl iodide, one gramme-molecule of the latter being employed for each gramme-atom of magnesium, a reaction ensues, the heat evolved raising the ether to the boiling-point. When sufficient ether is present, all the magnesium dissolves, forming an *alkyl magnesium iodide*, $C_nH_{2n+1}\cdot Mg\cdot I$. This is combined with one molecule of ether, because on evaporation to dryness the residue still contains equimolecular proportions of ether and the metallic compound.

The alkyl magnesium halides of the type $R\cdot Mg\cdot X$ can also be obtained free from ether by dissolving the alkyl halide in benzene, light petroleum, and other solvents, adding magnesium, and inducing the reaction by the introduction of a small quantity of a tertiary amine or of ether as a catalyst.

Unlike the zinc alkides, the alkyl magnesium halides do not ignite spontaneously when brought into contact with air. They are often employed for syntheses, notably those of the secondary and tertiary alcohols (111).

The alkyl magnesium halides are decomposed by water, with formation of saturated hydrocarbons:

$$C_nH_{2n+1}\cdot Mg\cdot Cl+H_2O=C_nH_{2n+2}+Mg(OH)Cl.$$

Mercury alkides are prepared similarly to zinc alkides. They do not ignite in the air, and are dangerously poisonous. Such compounds as $C_2H_5 \cdot Hg \cdot OH$ are weak bases.

Alkyl-derivatives of beryllium, magnesium, cadmium, aluminium, thallium, and lead have also been obtained, some by the aid of GRIGNARD's alkyl magnesium halides. A typical instance is the formation of tin ethide by the interaction of stannic bromide and ethyl magnesium bromide:

$$SnBr_4 + 4C_2H_5 \cdot Mg \cdot Br = Sn(C_2H_5)_4 + 4\,MgBr_2.$$

NITRILES AND ISONITRILES.

83. When potassium ethylsulphate is distilled with potassium cyanide or anhydrous potassium ferrocyanide, $K_4Fe(CN)_6$, a liquid of exceedingly unpleasant odour is obtained. By fractional distillation it can be separated into two substances, both with the formula C_3H_5N. One is called *ethylcarbylamine*, and is only present in small proportion: it boils at 82°, and has a disagreeable smell like that of the original mixture. The other constitutes the main portion, and is called *ethyl cyanide:* it boils at 97°, and after purification has a not unpleasant odour, which is much less penetrating than that of ethylcarbylamine.

When acted upon by inorganic acids, these isomerides yield quite different decomposition-products. Ethylcarbylamine is attacked at ordinary temperatures: the oily layer floating on the surface of the acid dissolves completely, and the disagreeable odour disappears. *Formic acid*, CH_2O_2, can be obtained from this solution by distillation; and on addition of caustic potash to the residue in the distilling-flask and subsequent distillation, ethylamine, $C_2H_5NH_2$, passes over, indicating that the nitrogen atom in ethylcarbylamine, C_3H_5N, is directly united with the ethyl-group:

$$\underset{\text{Ethylcarbylamine}}{C_3H_5N} + 2H_2O = \underset{\text{Formic acid}}{CH_2O_2} + \underset{\text{Ethylamine}}{C_2H_5NH_2}.$$

Ethyl cyanide is only slowly attacked by inorganic acids at ordinary temperatures, but heating accelerates their action. On warming the mixture in a flask with a reflux-condenser and subsequent distillation, *propionic acid*, $C_3H_6O_2$, passes over. This acid contains the same number of carbon atoms as ethyl cyanide, C_3H_5N. On making the residue in the flask alkaline and again distilling, ammonia is obtained. The nitrogen atom in ethyl cyanide cannot, therefore, be in direct union with the ethyl-group:

$$\underset{\text{Ethyl cyanide}}{C_3H_5N} + 2H_2O = \underset{\text{Propionic acid}}{C_3H_6O_2} + NH_3.$$

These facts indicate that the nitrogen atom in ethylcarbylamine is in direct union with the ethyl-group, and that the three carbon atoms are not directly united, since one of them can be eliminated with production of formic acid. In ethyl cyanide, on the other hand, there must be a chain of three carbon atoms like that in propionic acid (87), and the nitrogen cannot be directly linked to the ethyl-group. These facts are expressed by the constitutional formulæ

$$\underset{\text{Carbylamine}}{\text{I. } C_2H_5—NC,} \qquad \underset{\text{Cyanide}}{\text{II. } C_2H_5—CN.}$$

On account of their method of formation, each must contain the group CN.

Compounds with a structural formula like I. are named *carbylamines* or *isonitriles;* those with a structural formula like II. are called *cyanides* or *nitriles*. The names of the former are derived from the alkyl-radical they contain, thus *methylcarbylamine, ethylcarbylamine,* etc. The latter can be designated analogously *methyl cyanide, ethyl cyanide*, etc., but are usually called *nitriles* and are named after the acid from which they are derived. Thus $CH_3 \cdot CN$ is *acetonitrile*, and $C_2H_5 \cdot CN$ *propionitrile*, and so on.

The constitution of the groups —CN and —NC requires further consideration. They are represented as $—C \equiv \overset{III}{N}$ and $—\overset{V}{N} \text{≣} C$, the first with a triple, and the second with a quadruple, bond between C and N. The reasons for adopting these formulæ in preference to such a one, for example, as $—\underset{\|}{C}—N=$ with free affinities are stated in 128.

The existence of a bivalent carbon atom in the carbylamines in a group $—\overset{III}{N}=\overset{II}{C}$ is assumed by Nef and some other chemists (*cf.* 135 and 427).

Carbylamines.

84. Carbylamines are the principal product of the interaction of alkyl iodides and silver cyanide. They can also be obtained unmixed with nitriles by the action of caustic potash and chloroform, $CHCl_3$, upon primary amines:

$$C_2H_5N\boxed{H_2 + C}\boxed{HCl_3} + 3KOH = 3KCl + 3H_2O + C_2H_5 \cdot NC.$$

On account of the disagreeable and characteristic odour of the carbylamines, this reaction affords an exceedingly delicate test for primary amines. Secondary and tertiary amines are not converted into carbylamines by this reaction, since they lack *two* hydrogen atoms in direct union with the nitrogen atom of the amine.

The carbylamines are colourless liquids, very stable towards alkalis, but readily converted by acids into a primary amine and formic acid. With dry hydrochloric acid in ethereal solution they yield unstable addition-products, such as $2CH_3NC \cdot 3HCl$.

Nitriles.

85. Nitriles are the chief product obtained when potassium cyanide reacts with alkyl iodides (*cf.* 84), or when it is submitted to dry distillation with potassium alkylsulphate. Sometimes anhydrous potassium ferrocyanide, $K_4Fe(CN)_6$, can be advantageously substituted for potassium cyanide.

Nitriles can be prepared by the action of an alkaline bromine solution (German, *Bromlauge*) on the higher primary amines:

$$C_7H_{15}CH_2 \cdot NH_2 + 2Br_2 + 2NaOH = C_7H_{15}CH_2 \cdot NBr_2 + 2NaBr + 2H_2O;$$

$$C_7H_{15}C\boxed{H_2}N\boxed{Br_2} + 2NaOH = C_7H_{15}CN + 2NaBr + 2H_2O.$$

The nitriles are liquids of characteristic odour, soluble in water, and having specific gravities about 0·8. They are converted not only by acids, but also by warming with alkalis, into fatty acids containing the same number of carbon atoms and ammonia, a process called *hydrolysis*. They form addition-products with many substances, by conversion of the triple bond between nitrogen and carbon into a single bond. An example of this reaction is the addition of nascent hydrogen (MENDIUS):

$$C_2H_5 \cdot CN + 4H = C_2H_5 \cdot CH_2 \cdot NH_2.$$

This produces a primary amine (71) with the same number of carbon atoms as the nitrile, the yield being very good for the higher members when sodium is brought into contact with a mixture of the nitrile and boiling absolute alcohol.

A description of a number of other addition-products of the nitriles is given in 105.

ACIDS, $C_nH_{2n}O_2$.

86. A solution of a sodium alkide in zinc alkide is obtained by the interaction of sodium and a zinc alkide (**82**). When a stream of dry carbon dioxide is passed into this solution, the sodium salt of an acid with one carbon atom more in the molecule than the alkyl-group is formed. Thus, sodium methide, CH_3Na, yields sodium acetate, $C_2H_3O_2Na$. This reaction may be explained by assuming that the sodium atom is released from the alkyl-group, and reacts with CO_2, becoming linked to an oxygen atom, an element for which it possesses great affinity: $\mathrm{C}\begin{array}{l}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow\!\!\!\!\searrow \mathrm{O}\end{array}$ is thus converted into $-\mathrm{C}\begin{array}{l}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow \mathrm{ONa}\end{array}$. Since this group, and also the alkyl-radical from which the sodium atom has been separated, have one free carbon bond apiece, it may be assumed that the two groups unite, forming a compound

$$\mathrm{C_nH_{2n+1}}-\mathrm{C}\begin{array}{l}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow \mathrm{ONa}.\end{array}$$

Analogous to this is the formation of acids by the interaction of GRIGNARD's alkyl magnesium halides (82) and carbon dioxide:

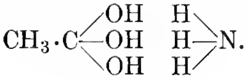
$$CH_3{\cdot}Mg{\cdot}Br + CO_2 = \underset{\text{Addition-product}}{CH_3{\cdot}CO{\cdot}O{\cdot}Mg{\cdot}Br.}$$

The addition-product is decomposed by water, with production of the acid:

$$CH_3{\cdot}CO{\cdot}O{\cdot}Mg{\cdot}Br + H_2O = CH_3{\cdot}CO{\cdot}OH + Mg(OH)Br.$$

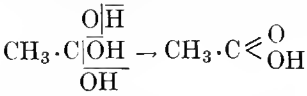
In accordance with these reactions the acids $C_nH_{2n}O_2$ contain the group $-\mathrm{C}\begin{array}{l}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{array}$ in union with an alkyl-radical. This view is supported by the formation of these compounds by other methods.

Among them is their synthesis by the interaction of an alkyl iodide and potassium cyanide, followed by hydrolysis of the resulting nitrile. This hydrolysis consists in the addition of the elements of water, and entails breaking the bonds between carbon and nitrogen in the group $—C \equiv N$. If any other bond in a nitrile $CH_3 \cdot CH_2 \cdot CH_2 \ldots . CN$ were released, it would involve a severance of the carbon chain, and prevent the formation of an acid containing the same number of carbon atoms as the nitrile. The hydrolysis of the nitrile, in which an acid and ammonia are formed, may therefore be explained by assuming that the molecules of water are resolved into H and OH, the hydroxyl uniting with the carbon, and the hydrogen with the nitrogen. By a threefold repetition of this the nitrogen is converted into ammonia, the three bonds between carbon and nitrogen, in the nitrile, being severed:



$$CH_3 \cdot C \begin{cases} OH \\ OH \\ OH \end{cases} \quad \begin{matrix} H \\ H \\ H \end{matrix} \Big\rangle N.$$

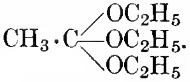
The formula of the acid formed is not $CH_3 \cdot CO_3H_3$, but $CH_3 \cdot CO_2H$, containing one molecule of water less. When one molecule of water is eliminated from $CH_3 \cdot CO_3H_3$, there results



$$CH_3 \cdot C \begin{matrix} O|\overline{H} \\ |\underline{OH} \\ OH \end{matrix} \rightarrow CH_3 \cdot C \lessdot \begin{matrix} O \\ OH \end{matrix},$$

a substance containing the *carboxyl-group.*

In this explanation of the formation of acids, the existence of an intermediate compound containing three hydroxyl-groups is assumed. Such substances are not known, but the assumption seems by no means improbable, because compounds containing three alkoxyl-groups exist; for example,



$$CH_3 \cdot C \begin{cases} OC_2H_5 \\ OC_2H_5. \\ OC_2H_5 \end{cases}$$

They are called *ortho-esters* (155).

The acids $C_nH_{2n}O_2$ can be formed by the action of carbon monoxide on metallic alkoxides under the influence of heat:

$$CH_3 \cdot ONa + CO = CH_3 \cdot COONa.$$

The formation of an addition-product between $CH_3 \cdot ONa$ and CO can be explained by the assumption that the alkoxide first decomposes into CH_3 and ONa.

It is mentioned in 49 and 50 that oxidation converts the primary alcohols into acids of the general formula $C_nH_{2n}O_2$, with the same number of C-atoms in the molecule. In this reaction the group —CH_2OH is oxidized to —COOH.

The higher primary alcohols can also be transformed into the corresponding acids by heating them with soda-lime, free hydrogen being evolved:

$$\underset{\text{Stearyl alcohol}}{C_{17}H_{35}\cdot CH_2OH} + NaOH = \underset{\text{Sodium stearate}}{C_{17}H_{35}\cdot COONa} + 2H_2$$

The presence of hydroxyl in the carboxyl-group is proved by the action of the chlorides of phosphorus, which replace the OH-group by Cl, as with the alcohols.

In each molecule of the acids of this series there is one hydrogen atom replaceable by metals. Only the carboxyl-hydrogen atom is in direct union with oxygen, and its special position suggests that it is the replaceable atom. The truth of this supposition has been proved by treating silver acetate, $C_2H_3O_2Ag$, with ethyl iodide: ethyl acetate is formed, and not butyric acid, which would result if the Ag-atom were attached to the methyl C-atom; thus, $CH_2Ag\cdot COOH$.

87. The lower members of this series of acids are liquid at ordinary temperatures. They can be distilled without decomposition, and have a very irritating and strongly acid odour in the concentrated state. They are miscible in all proportions with

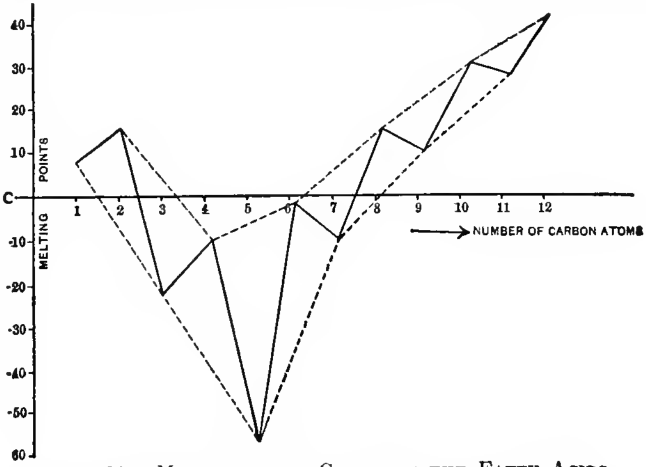


Fig. 29.—Melting-point Curve of the Fatty Acids.

water. The middle members (C_4—C_9) have a disagreeable rancid smell. They are of an oily nature, and do not mix with water in all proportions. The higher members, beginning at C_{10}, are solid at ordinary temperature, without odour, and resemble paraffin-wax in character. They are almost insoluble in water, and cannot be distilled at the atmospheric pressure without decomposition. All the acids of this series dissolve readily in alcohol and ether. Except the first member, they are very stable towards oxidizing agents.

The acids of the series $C_nH_{2n}O_2$ are called *fatty acids*, some of the higher members having been first obtained from fats.

Many of the fatty acids are natural products, occurring either in the free state or as esters, and are of great theoretical and technical importance. The table contains the names, formulæ, and certain physical constants of the normal-chain acids of the series $C_nH_{2n}O_2$.

Name.	Formula.	Melting-point.	Boiling-point	Specific Gravity.
Formic acid......	CH_2O_2	8·3°	101°	1·2310 (10°)
Acetic acid.......	$C_2H_4O_2$	16·598°	118°	1·0515 (15°)
Propionic acid....	$C_3H_6O_2$	−22°	141°	0·9985 (14°)
Butyric acid......	$C_4H_8O_2$	− 7·9°	162°	0·9599 (19·1°)
Valeric acid......	$C_5H_{10}O_2$	−58·5°	186°	0·9560 (0°)
Caproïc acid......	$C_6H_{12}O_2$	− 1·5°	205°	0·9450 (0°)
Heptylic acid.....	$C_7H_{14}O_2$	−10·5°	223°	0·9186 (17·2°)
Caprylic acid.....	$C_8H_{16}O_2$	16·5°	237·5°	0·9100 (20°)
Nonylic acid......	$C_9H_{18}O_2$	12·5°	254°	0·9110 (M.P.)
Capric acid.......	$C_{10}H_{20}O_2$	31·4°	269°	
Palmitic acid.....	$C_{16}H_{32}O_2$	62·618°		
Margaric acid.....	$C_{17}H_{34}O_2$	60°		
Stearic acid......	$C_{18}H_{36}O_2$	69·32°		

Although the boiling-points rise with increase in the number of C-atoms in the molecule, the melting-points of the acids with an even number of C-atoms are higher than those of the acids immediately preceding and succeeding them, with an odd number of C-atoms (Fig. 29). This phenomenon has also been observed in some other homologous series.

The residual groups which would result by elimination of hydroxyl from fatty-acid molecules are unknown in the free state, but named after the corresponding acids by changing the termination "ic" into "yl"; thus,

$\mathrm{H{\cdot}CO}$ Formyl,
$\mathrm{CH_3{\cdot}CO}$ Acetyl,
$\mathrm{C_2H_5{\cdot}CO}$ Propionyl,
$\mathrm{C_3H_7{\cdot}CO}$ Butyryl,
$\mathrm{C_4H_9{\cdot}CO}$ Valeryl,
etc.

Formic Acid, $\mathrm{H{\cdot}COOH}$.

88. *Formic acid* derives its name from its presence in ants (Latin, *formica*). It can be obtained by passing carbon monoxide over soda-lime at 210°, the yield being good (**86**), but is usually prepared by another method (**158**). It can also be got by oxidizing methyl alcohol. A peculiar method of synthesis is to pass a silent electric discharge through a mixture of carbon monoxide and steam, or carbon dioxide and hydrogen.

Pure formic acid is a colourless liquid of irritating odour. Its salts are called *formates:* they are soluble in water, some only with difficulty.

Formic acid is distinguished from its homologues: first, by its susceptibility to oxidation, and hence its reducing power; second, in being readily decomposed into carbon monoxide and water. When mercuric oxide is added to a solution of formic acid, a solution of mercuric formate is obtained. If this solution be filtered and warmed, mercurous formate is precipitated with evolution of carbon dioxide, and on further warming, metallic mercury is liberated:

$$\mathrm{Hg}\,\underbrace{\frac{\mathrm{OOCH}\quad\mathrm{H\,COO}}{|\mathrm{OOCH}+\mathrm{H}|\mathrm{COO}|}}_{\text{Mercuric formate}}\mathrm{Hg} = \underset{\substack{\text{Mercurous}\\ \text{formate}}}{2\mathrm{HgOOCH}}+\mathrm{CO_2}+\mathrm{HCOOH};$$

$$\mathrm{Hg}\underbrace{\overline{|\mathrm{OOCH}+\mathrm{H}|\mathrm{COO}|}}_{\text{Mercurous formate}}\mathrm{Hg} = 2\mathrm{Hg}+\mathrm{CO_2}+\mathrm{HCOOH}.$$

In this process half of the formic acid in the salt is set free, and half is oxidized. When a solution of silver formate is warmed, an exactly analogous reaction takes place; metallic silver is precipitated, carbon dioxide evolved, and half of the acid liberated.

When formic acid is warmed with concentrated sulphuric acid, water and carbon monoxide are formed:

$$\boxed{\mathrm{H}}\mathrm{CO}\boxed{\mathrm{OH}}=\mathrm{H_2O}+\mathrm{CO}.$$

The introduction of finely powdered metallic rhodium into an aqueous solution of the acid effects this decomposition even at ordinary temperatures, the rhodium acting as an accelerating catalyst. Since reactions which do not take place spontaneously cannot be brought about by catalysis ("Inorganic Chemistry," **25**), it follows that formic acid decomposes of itself in the above sense, although so slowly as to seem perfectly stable. A large number of organic compounds behave similarly (*Ibid.*, **104**).

It is apparent that the properties of formic acid differ somewhat from those of the other acids of the homologous series in which it is the lowest member. A similar phenomenon is of frequent occurrence.

Acetic Acid, $CH_3 \cdot COOH$.

89. *Acetic acid* has been known longer than any other acid. It is manufactured by two different methods.

a. By oxidation of dilute alcohol, wine, beer, etc., by exposure to the air, with production of vinegar. The oxygen of the atmosphere acts upon the alcohol by the aid of bacteria, and the process must be so regulated that these bacteria produce the greatest possible effect. To this end it is important that the temperature should be kept between 20° and 35°.

In the "quick" or German process for the preparation of vinegar (Fig. 30), dilute alcohol (6–10 per cent.) is allowed to drop on beech-wood shavings contained in a vat with a perforated false bottom, *a*. Holes bored in the sides of the vat near the bottom serve to admit an ascending stream of air, opposite in direction to that of the alcohol. The shavings of beech-wood distribute the liquid over a very large surface, thus facilitating the oxidizing action of the air, while at the same time they serve as a feeding ground for the bacteria.

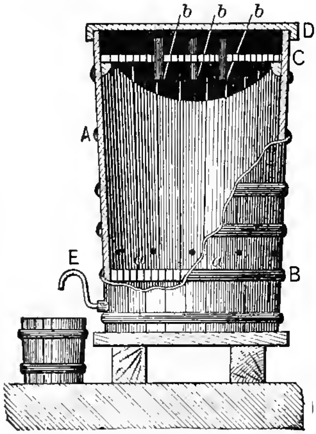


Fig. 30.—Preparation of Vinegar by the "Quick" or German Process.

b. Acetic acid is obtained in the distillation of wood (**46**). By treatment with quicklime, the acid is converted into calcium acetate, which is freed from tarry impurities by heating to 200° in the air. The acetic acid is then liberated by distilling with an equivalent quantity of concentrated hydrochloric acid. It can be purified by distillation from potassium dichromate, being very stable towards oxidizing agents.

Anhydrous acetic acid is solid at temperatures below 16·6°, when it has much the appearance of ice; hence the name *glacial* acetic acid. The solid acid has a penetrating odour, and is obtained by allowing a very concentrated solution of acetic acid to solidify, pouring off the liquid residue, melting the solidified acid, again allowing it to crystallize, and so on, these operations being repeated until the melting-point is constant. A rise of temperature and contraction of volume occur when glacial acetic acid is mixed with water, the maximum rise and contraction being produced by mixing in the proportion of one gramme-molecule of acetic acid to one gramme-molecule of water. This fact indicates the existence of a compound called *ortho-acetic acid* (**86**), with the formula $CH_3\cdot COOH\cdot H_2O = CH_3\cdot C(OH)_3$.

A fifty-five per cent. solution of glacial acetic acid in water has the same specific gravity as the pure, anhydrous acid. When water is added to glacial acetic acid, the specific gravity of the mixture first rises: further addition of water causes it to fall. This circumstance makes it impossible to determine the amount of acid present in such mixtures by the simple use of the hydrometer.

The strength of very concentrated acetic acid is best determined by an observation of its melting-point, a thermometer graduated in tenths of a degree being used. In accordance with the formula given in **12**,

$$\Delta M = \text{Constant},$$

the presence of 1 per cent. of water (molecular weight 18) would, since the constant for glacial acetic acid is 39, cause a depression (Δ) of $\frac{39}{18}$, or 2·16°. Since a thermometer graduated in tenths can easily be read to within one-twentieth of a degree, the amount of water can be determined to within $\frac{1}{2\cdot 16\times 20}$, or 0·025 per cent. This is a degree of accuracy unattainable by titration.

When either no very great accuracy is required, or the acetic acid is dilute, it is best to determine the strength by titrating a weighed quantity of the solution with a standard solution of alkali.

The vapour density of acetic acid at temperatures slightly above its boiling-point is twice as great as that corresponding to the formula $C_2H_4O_2$. At about 200°, however, the vapour density is normal. A similar phenomenon has been observed with many acids of this series and other substances (296).

The *acetates*, or salts of acetic acid, are soluble in water, the silver salt dissolving with difficulty. When ferric chloride is added to a solution of an acetate, such as sodium acetate, a blood-red colour is produced, owing to the formation of ferric acetate (the salts of formic and propionic acids produce the same result). When this solution is sufficiently dilute, brown-red basic ferric acetate, $Fe(OH)_2C_2H_3O_2$, is precipitated on boiling, acetic acid being simultaneously liberated.

The dry distillation of anhydrous sodium acetate with soda-lime produces methane:

$$CH_3\cdot COONa + NaOH = CH_4 + Na_2CO_3.$$

A very delicate test for acetic acid is the formation of cacodyl oxide (80). Owing to the extremely poisonous nature of this substance, great care must be exercised in applying the test. Among the acetates of technical importance are *lead acetate* ("sugar of lead"), *basic lead acetate*, and *aluminium acetate*. The first two are used in the manufacture of white lead, and the third as a mordant in calico-printing (362).

Butyric Acids, $C_4H_8O_2$.

90. Two isomeric acids with the formula $C_4H_8O_2$ are known. They are *normal butyric acid*, $CH_3\cdot CH_2\cdot CH_2\cdot COOH$, and iso*butyric acid*, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COOH$. The constitution of these acids is proved by their synthesis, the normal compound being obtained from *n*-propyl iodide, and the *iso*-acid from *iso*propyl iodide:

$$CH_3\cdot CH_2\cdot CH_2I \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot CN \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot COOH.$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CHI \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CN \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COOH.$$

The normal compound is also called "fermentation" butyric acid, from the fact that it can be obtained by the fermentation under certain conditions of such substances as sugar. It has an extremely disagreeable odour, and can only be oxidized with difficulty.

Butter contains about 4–5 per cent. of *n*-butyric acid, along with smaller quantities of other volatile acids of the fatty series, such as caproïc acid: they are probably present as esters. Since volatile fatty acids are not obtained by saponification of other fats, whether animal or vegetable, their presence furnishes the most characteristic distinction between butter and margarine: the latter is a mixture of animal and vegetable fats. Since the percentage of volatile fatty acids in butter is not a constant quantity, but may vary between wide limits, it is not always possible to determine that a sample of butter has been adulterated with margarine by estimating these acids. By the application of other tests, however, it is sometimes possible to decide in such doubtful cases.

iso*Butyric acid* also has a very disagreeable odour. It contains a tertiary carbon atom, and since such compounds are readily oxidized, oxidation affords a method of distinguishing between the normal acid and the *iso*-acid.

The calcium salts of these acids also exhibit a remarkable difference, that of the normal acid being less soluble in hot water than in cold, while that of the *iso*-acid follows the ordinary rule, and is more soluble in hot than in cold water. When heated to about 80°, a solution of normal calcium butyrate saturated at 0° deposits considerable quantities of the salt.

In accordance with the *principle of mobile equilibrium* ("Inorganic Chemistry," 235), calcium *n*-butyrate should dissolve in water with slight evolution of heat, and calcium *iso*butyrate with slight absorption of heat. This view is fully supported by the results of experiment.

Higher Fatty Acids, $C_nH_{2n}O_2$.

91. Many of the higher members of the series of fatty acids are natural products, chief among them being *palmitic acid*, $C_{16}H_{32}O_2$, and *stearic acid*, $C_{18}H_{36}O_2$, both with normal carbon chains (144). In the form of esters of glycerol (159), these two acids occur in large quantities as the principal constituent of most animal and vegetable fats, from which they are obtained by saponification, a process carried out by heating either with slaked lime (**101**), or with concentrated sulphuric acid. The latter causes slight carbonization, imparting a dark colour to the fatty acids. They can be purified by distillation with superheated steam.

> Another method of decomposing the fats into glycerol and a fatty acid depends upon the action of an enzyme (**219**) present in castor-seed (Latin, *ricinus communis*). After removal of the oil, the powdered seeds are intimately mixed with the fat: on addition of a dilute acid, such as decinormal sulphuric acid, an emulsion is formed. If the mixture is kept at a temperature of 30°–40° for two or three days, the fatty acids are set free in a very pure state; on gentle heating, the emulsion then separates into two layers, the upper consisting of the free acids, and the lower of an aqueous solution containing 40–50 per cent. of glycerol.

Saponification of fats yields a mixture of acids, semi-solid at ordinary temperatures. This mixture contains the two acids mentioned above, melting at 62° and 69° respectively, when pure; but when mixed, each lowers the melting-point of the other (**26**). Moreover, liquid oleïc acid, belonging to another homologous series, is also present: it can be pressed out of the mixture, leaving a white, solid substance used in the manufacture of "stearine" candles. For this purpose the "stearine" is melted, and after addition of a small proportion of paraffin-wax, to prevent crystallization of the fatty acids, which would make the candles brittle, the molten substance is poured into moulds, in the axes of which wicks are fastened.

Soaps consist chiefly of the alkali-metal salts of the acids contained in fats. They are prepared by saponifying fats with a solution of caustic soda or of caustic potash heated to the boiling-temperature. Potassium-soap is called "soft soap," and is usually yellow. In some countries it is tinted green by the addition of indigo, and is then known as "green soap." Potassium-soap contains not only the potassium salts of the acids, but also the glycerol produced in the reaction, and a considerable proportion of water. Sodium-soap is hard: it is separated from the reaction-mixture, after saponification is complete, by "salting-out," which consists in the addition of solid common salt to the mixture at the boiling-temperature. Since the sodium salts of the acids are insoluble in a concentrated solution of sodium chloride, the soap separates out in the molten state, forming a layer on the surface of the brine, in which the glycerol remains dissolved. The soap thus obtained consists of the sodium salts of the acids, with a small percentage of water.

92. The cleansing action of soap may be explained as follows. When an alkali-metal salt of one of the higher fatty acids is brought into contact with a large excess of water, it decomposes with formation of free alkali, a fact that was pointed out by CHEVREUL as early as at the beginning of the nineteenth century. The acid thus liberated unites with a second molecule of the salt to form an insoluble substance, which with the water produces the lather. The presence of free alkali in dilute soap-solutions can be experimentally demonstrated. A concentrated soap-solution is only very slightly coloured by phenolphthaleïn; but the addition of a large proportion of water causes the development of the red colour, due to the action of the base thus liberated on the phenolphthaleïn. The soap has therefore undergone hydrolytic dissociation, owing to the weak acidic character of the higher fatty acids.

The soiling of the skin, clothing, etc., is usually due to substances of a fatty nature. When a fat is agitated with an alkaline liquid, part of the fat is saponified, and dissolves. The greater portion, however, remains suspended in the form of minute drops, yielding a liquid of milky appearance called an emulsion. The alkali liberated from the soap has therefore both a saponifying and an emulsifying action on the substance to which the soiling is due.

This being admitted, the use of soap in preference to free alkali for washing demands explanation. This is found in the fact that the use of soap prevents the presence of an excessive proportion of free alkali. The proportion of alkali liberated from soap is small with a small quantity of water, and large with a large quantity. Hence the addition of a large quantity of water does not greatly affect the concentration—the amount of free alkali in unit volume of liquid—since, although it produces much free alkali, it simultaneously dilutes it. The use of soap has therefore the effect of automatically regulating the proportion of free alkali present in the water, keeping it small. There would be no such adjustment if free alkali were employed instead of soap: the latter possesses the further advantage of forming a lather, which takes up the dirt and thus facilitates its removal.

Water containing a certain percentage of calcium salts is called a "hard" water ("Inorganic Chemistry," 259). Such water does not immediately lather with soap, but causes the formation of a white, flocculent substance, consisting of insoluble calcium salts of the fatty acids. Hard water is therefore unsuitable for washing, because it prevents the formation of a lather, and also because the alkali is neutralized and thus withdrawn by the acid-radical of the calcium salts (sulphate and carbonate) present.

Electrolytic Dissociation.

93. Molecules of acids, bases, and salts are assumed to be resolved, on solution in water, into ions, charged with opposite kinds of electricity ("Inorganic Chemistry," 65 and 66). In such a solution, an acid is partially or completely dissociated into positively charged hydrogen ions, $H^{\cdot}$ (cathions), and negatively charged anions: for example, acetic acid is resolved into $H^{\cdot}$ (positive), and $(C_2H_3O_2)'$ (negative). Bases yield a positively charged metallic ion, and a negatively charged OH'-ion; salts a positively charged metallic ion, and a negatively charged acid-radical ion.

It is further stated (*Ibid.*, 66) that in the solution of a partly ionized substance there is an equilibrium which for a monobasic acid can be expressed by

$$ZH \rightleftarrows Z' + H^{\cdot},$$

where Z' represents the acid-radical. If v is the volume in litres containing one gramme-molecule of the acid, and α is the portion ionized, then the concentration of the ions is $\frac{\alpha}{v}$, and that of the non-ionized portion is $\frac{1-\alpha}{v}$. The equation representing the equilibrium in the above example of a monobasic acid is, therefore (*Ibid.*, 49),

$$k\frac{1-\alpha}{v} = \left(\frac{\alpha}{v}\right)^2, \text{ or } \frac{\alpha^2}{v(1-\alpha)} = k.$$

In this equation k is constant, and is called the *ionization-constant.* It has been proved that this equation affords an exact measure of the amount of ionization for the very weak organic acids; that is, expresses accurately the connection between the dilution v and the ionization α. For this reason it is called the *law of dilution.*

It was discovered by Ostwald, who dissolved one gramme-molecule of an acid in different quantities of water, v, and ascertained the ionizations α by determining the electric conductivity. On substituting the values obtained for α and v respectively in the expression $\frac{\alpha^2}{v(1-\alpha)}$, the latter was always found to have the same value, as it must if k is constant.

The accuracy of this law is evident from the examples in the following table.

Acetic Acid.			Propionic Acid.			*n*-Butyric Acid.		
v	$100a$	10^4k	v	$100a$	10^4k	v	$100a$	10^4k
8	1·193	0·180	8	1·016	0·130	8	1·068	0·144
16	1·673	0·179	16	1·452	0·134	16	1·536	0·150
32	2·380	0·182	32	2·050	0·134	32	2·165	0·149
64	3·33	0·179	64	2·895	0·135	64	3·053	0·150
128	4·68	0·179	128	4·04	0·133	128	4·292	0·150
1024	12·66	0·177	1024	10·79	0·128	1024	11·41	0·144

94. The "strength" of acids depends upon their degree of ionization, strong acids undergoing considerable, and weak acids but slight, ionization. Since the constant k rises or falls in value simultaneously with α, and is independent of the concentration, it affords a convenient measure of the strength of an acid.

The table shows the values of 10^4k for certain fatty acids.

Formic	Acetic	Propionic	*n*-Butyric	Valeric
2·14,	0·18,	0·13,	0·15,	0·16.

It is noteworthy that formic acid has a greater ionization-constant, and is therefore stronger, than its homologues, another example of the difference between it and the other members of the series.

A comparison of these acids with such strong mineral acids as sulphuric acid and hydrochloric acid, from the point of view of the magnitude of their ionization-constants, shows that the former are very much weaker than the latter. When $v=16$, then for hydrochloric acid $100\alpha=95{\cdot}55$, and for acetic acid only 1·673. It is obvious that 100 α is the amount ionized, expressed in percentage.

The weak organic acids follow the law of dilution : the strong mineral acids do not. No perfectly satisfactory explanation of this phenomenon has been suggested hitherto.

DERIVATIVES OF THE FATTY ACIDS OBTAINED BY MODIFYING THE CARBOXYL-GROUP.

95. The carboxyl-group may be modified by the exchange of its oxygen atoms or hydroxyl-group for other elements or groups. The compounds described in this chapter contain such modified carboxyl-groups.

I. Acid Chlorides.

Acid chlorides are derived from acids by replacement of the hydroxyl-group by chlorine, and consequently contain the group —COCl. They are obtained from the acids by the action of the chlorides of phosphorus, PCl_5 and PCl_3, or of phosphorus oxychloride, $POCl_3$:

$$3C_nH_{2n+1}\cdot COOH+2PCl_3 = 3C_nH_{2n+1}\cdot COCl+P_2O_3+3HCl.$$

The ease with which the acid chlorides are converted into the corresponding acids is a proof that the chlorine atom has replaced the hydroxyl-group. For the lower members this conversion is effected by merely bringing them into contact with water. If the chlorine atom had substituted hydrogen of the alkyl-group, there would be no reaction, since an alkyl chloride is not decomposed by water at ordinary temperatures.

The acid chlorides of this series, at least the lower members, are liquid, and have a suffocating, irritating odour. The chloride corresponding to formic acid is not known. *Acetyl chloride*, CH_3COCl, fumes in the air, and can be distilled without decomposition. It boils at 55°, and its specific gravity is 1·13 at 0°.

Acetyl chloride is employed in detecting the presence of hydroxyl in organic compounds. Hydroxyl is replaced by acetyl: thus, alcohols form esters of acetic acid:

$$R\cdot O\boxed{H+Cl}OC\cdot CH_3 = RO\cdot OC\cdot CH_3+HCl.$$

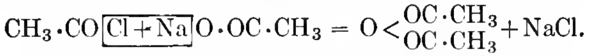
The compound to be tested is allowed to remain for some time in contact with acetyl chloride, either at the ordinary temperature or with gentle warming. To ascertain whether an acetyl-compound has been formed, the purified product is analyzed or saponified. If saponification yields acetic acid, an acetyl-derivative was present.

The homologues of acetyl chloride are also sometimes employed in the detection of hydroxyl-groups.

The acid chlorides also react with the mercaptans, forming substances of the type of acetyl-compounds.

II. Acid Anhydrides.

96. *Acid anhydrides* are formed by interaction of the alkali-metal salts of acids and acid chlorides:



$$CH_3{\cdot}CO\boxed{Cl+Na}O{\cdot}OC{\cdot}CH_3 = O{<}\begin{matrix}OC{\cdot}CH_3\\OC{\cdot}CH_3\end{matrix}+NaCl.$$

Acetic anhydride

Higher anhydrides are best obtained by heating the sodium salts of the higher acids with acetic anhydride.

The acid chlorides may be regarded as mixed anhydrides of hydrochloric acid and an acid, a view supported by their formation from these two acids by treatment with phosphorus pentoxide as a dehydrating agent.

Mixed anhydrides of the fatty acids themselves exist, although when distilled they decompose into the anhydrides of the two acids.

The lower members of this series are liquids, and have a disagreeable, suffocating odour. *Acetic anhydride* boils at 137°, and has a specific gravity of 1·073 at 20°. At ordinary temperatures it is soluble in about ten times its volume of water, the solution decomposing slowly with formation of acetic acid. In this respect it differs from acetyl chloride, which reacts momentarily and vigorously with water, yielding acetic acid and hydrochloric acid. Like acetyl chloride it is used in testing for the presence of the hydroxyl-group. No anhydride of formic acid is known.

III. Esters.

97. *Esters* result from the interaction of acid chlorides, or anhydrides, and alcohols:

$$CH_3{\cdot}CO\boxed{Cl+H}OC_2H_5 = CH_3{\cdot}COOC_2H_5+HCl.$$

They are also formed by direct treatment of the alcohol with the acid, although extremely slowly at ordinary temperatures:

$$CH_3{\cdot}COOH + HOC_2H_5 = CH_3{\cdot}COOC_2H_5 + H_2O.$$

The velocity of the reaction is much increased by a rise of temperature. Esters are also obtained by the action of the silver salt of an acid upon an alkyl iodide.

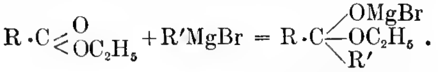
The following is a characteristic method frequently used for the preparation of these compounds. Dry hydrochloric-acid gas is passed through a mixture of absolute alcohol and the anhydrous organic acid. After some time the reaction-mixture is poured into water, whereupon the ester separates out, owing to its slight solubility. The formation of esters in this manner may be explained on the assumption that a very small quantity of the hydrochloric acid unites with the organic acid, water being eliminated, and a minute quantity of the acid chloride formed:

$$CH_3{\cdot}COOH + HCl = CH_3{\cdot}COCl + H_2O.$$

It is true that for each molecule of acid chloride formed in accordance with this equation an equivalent quantity of water is produced, sufficient to reconvert the chloride into the acid and hydrochloric acid. There is, however, such an infinitely greater number of molecules of alcohol than of water with which the chloride can react, that the probability of the formation of an ester is very much greater than the probability of the regeneration of the acid. The preponderance continues so long as the proportion of alcohol present greatly exceeds that of the water formed; so that when the object is to obtain the maximum yield of ester, the organic acid should be dissolved in a large excess of alcohol. The formation of esters is called *esterification.*

The esters are colourless liquids of neutral reaction, and do not mix with water in all proportions. They are lighter than water, most of them having a specific gravity between 0·8 and 0·9. Many of them are characterized by their agreeable odour, resembling that of fruits, a property which finds practical application in their employment in the manufacture of artificial fruit-essences. For example. iso*amyl* iso*valerate* (B.P. 196°) has an odour of apples, *ethyl butyrate* (B.P. 121°) of pineapples, iso*amyl acetate* (B.P. 148°) of pears, and so on.

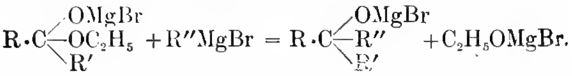
Tertiary alcohols can be synthesized from the esters by means of **Grignard**'s alkyl magnesium halides (82):



$$R\cdot C\begin{matrix}\nearrow O \\ \searrow OC_2H_5\end{matrix} + R'MgBr = R\cdot C\begin{matrix}\nearrow OMgBr \\ -OC_2H_5 \\ \searrow R'\end{matrix}.$$

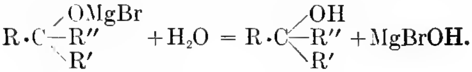
Addition-product

The addition-product thus obtained reacts with a second molecule of the alkyl magnesium halide.



$$R\cdot C\begin{matrix}\nearrow OMgBr \\ -OC_2H_5 \\ \searrow R'\end{matrix} + R''MgBr = R\cdot C\begin{matrix}\nearrow OMgBr \\ -R'' \\ \searrow R'\end{matrix} + C_2H_5OMgBr.$$

On decomposition with water the tertiary alcohol is formed:



$$R\cdot C\begin{matrix}\nearrow OMgBr \\ -R'' \\ \searrow R'\end{matrix} + H_2O = R\cdot C\begin{matrix}\nearrow OH \\ -R'' \\ \searrow R'\end{matrix} + MgBrOH.$$

R, R′, and R″ represent alkyl-groups

98. The formation of esters has been carefully investigated by several chemists, first of whom were Berthelot and Péan de St. Gilles. Their researches have shown that the reaction between the acid and the alcohol is never complete, some of both remaining uncombined no matter how long the process has been carried on. With equivalent quantities of acetic acid and ethyl alcohol, for example, the final product is such that from each gramme-molecule of alcohol and acid used, only two-thirds of a gramme-molecule of an ester and of water are formed, while one-third of a gramme-molecule of the alcohol and of the acid respectively remain uncombined. The same limit is reached when equivalent quantities of an ester and water are brought into contact. An *equilibrium* between the four substances, alcohol, acid, ester, and water, is ultimately reached, and is due to the *reversibility* of the reaction ("Inorganic Chemistry," 49). It may be represented as follows:

$$C_2H_5\cdot OH + CH_3\cdot CO\cdot OH \rightleftarrows CH_3\cdot CO\cdot OC_2H_5 + H_2O.$$

The equation of equilibrium deduced in *Ibid.*, 49 and 50, may be applied to the formation and decomposition of esters. It is

$$k(p-x)(q-x) = k'x^2, \quad \text{or} \quad (p-x)(q-x) = Kx^2,$$

where p is the initial concentration of the alcohol and q that of the acid, while x represents the quantities of water and of ester respectively present when the equilibrium is attained. All these are expressed in gramme-molecules, and K is a constant. There are here two opposing reactions taking place simultaneously, so that all the statements referred to above (*loc. cit.*) are applicable to the present instance. Given p, q, and K, the unknown quantity x can be calculated.

Numerous observations have proved that K is equal to 0·25 for the system *ethyl alcohol*+*acetic acid*. When one gramme-molecule of alcohol (46 g.) and one gramme-molecule of acetic acid (60 g.) are brought into contact, both p and q are equal to 1, and the equation is

$$(1-x)^2 = 0{\cdot}25x^2, \quad \text{or} \quad x^2 - \tfrac{8}{3}x + \tfrac{4}{3} = 0,$$

so that

$$x = \tfrac{2}{3}.$$

It follows that this system in equilibrium contains $\frac{1}{3}$ *gramme-molecule alcohol*+$\frac{1}{3}$ *gramme-molecule acetic acid*+$\frac{2}{3}$ *gramme-molecule water*+ $\frac{2}{3}$ *gramme-molecule ester*.

99. Several deductions can be drawn from the equation

$$(p-x)(q-x) = Kx^2.$$

These deductions had been established by experiment long before the development of the theory.

1. The esterification is approximately quantitative only when either the acid or the alcohol is largely in excess.

Putting the equation in the form

$$\frac{p-x}{x} = K\frac{x}{q-x},$$

it is evident that when the quantity of alcohol (p) is infinitely great, the left-hand side $= \infty$. This is true of the right-hand side when $q=x$, that is, when all the acid has been converted into ester. It also holds when the ratio of the quantity of acid to alcohol is infinitely great, the whole of the alcohol changing into ester.

Although these considerations indicate that esterification can be complete only in presence of an infinitely great excess of acid or alcohol, in practice the very nearly theoretical yield of ester is obtained when the ratio of the quantity of acid to alcohol, or of alcohol to acid, is finite. As can be readily deduced from the equation, this holds for the formation of ethyl acetate when one gramme-molecule of acid reacts with ten gramme-molecules of alcohol, or, inversely, when one gramme-molecule of alcohol reacts with ten gramme-molecules of acid.

2. The alcohol and the acid exercise the same influence on the formation of esters: thus, if a mixture containing a certain number of acid molecules is prepared and n times as many alcohol molecules, and another with the proportions of acid and alcohol reversed, then the number of molecules of acid converted into ester in the first mixture is equal to that of the molecules of alcohol converted in the second.

When p gramme-molecules of alcohol are mixed with np gramme-molecules of acid, the equation becomes

$$\frac{p-x}{x} = K\frac{x}{np-x}.$$

Inversely, when np gramme-molecules of alcohol are added to p gramme-molecules of acid, we have

$$\frac{np-x}{x} = K\frac{x}{p-x}.$$

These two equations are identical.

3. The addition of a quantity of the ester to the mixture of the alcohol and the acid at the beginning of the experiment has the same effect on the formation of ester as would be exerted by an equivalent quantity of water.

When r gramme-molecules of water or of ester are added to a mixture containing p gramme-molecules of alcohol and q gramme-molecules of acid, then for both the equation becomes

$$(p-x)(q-x) = Kx(x+r).$$

It follows that the equilibrium is influenced to the same extent by the addition of equivalent quantities of water or of ester.

100. A typical application of the principle of mobile equilibrium ("Inorganic Chemistry," 235) may be made to the formation of esters. Although the velocities of formation and decomposition of esters depend greatly upon the temperature, a change in the latter

has very small effect upon the equilibrium. At 10° the limit of esterification is 65·2 per cent.; at 220° it is 66·5 per cent. In accordance with the principle of mobile equilibrium, this necessitates that the heat of formation of the ester should be very small. That it actually is so has been established by experiment.

101. The conversion of an ester into an acid and an alcohol by a mineral acid or an alkali is called *saponification*, from analogy to the formation of soap from alkali and fat (**91**). It is represented by an equation of the type

$$CH_3 \cdot COOC_2H_5 + H_2O = CH_3 \cdot COOH + C_2H_5OH.$$

The action of the mineral acid is therefore catalytic. Its presence only accelerates the saponification: the same result would be attained without it, though the time required would be incomparably longer (**88**). If the concentration of the ester be C_1, that of the water is C_2, and x the quantity of ester saponified during the time t, then the velocity of saponification $S = \frac{dx}{dt}$ for each moment can be represented by the equation for bimolecular reactions ("Inorganic Chemistry," **50**):

$$S = \frac{dx}{dt} = k(C_1 - x)(C_2 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the ester is dissolved in a very large proportion of water, the concentration C_2 of the water is only very slightly altered by the saponification, so that it may be included in the constant. The equation is therefore simplified to that for a unimolecular reaction:

$$\frac{dx}{dt} = k_1(C_1 - x). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The saponification of esters by bases can be represented by an equation of the type

$$CH_3 \cdot COOC_2H_5 + NaOH = CH_3 \cdot COONa + C_2H_5OH.$$

It is a bimolecular reaction, and consequently equation (1) is applicable to it.

The velocity of saponification of esters by acids depends largely upon the acid, being greater the stronger the acid used. It has been proved that the velocity of saponification depends upon the extent of electrolytic dissociation of the acid employed. From this fact it may be concluded that the saponifying action is due to the hydrogen ion common to all acids. The velocity with bases is much greater than with acids; thus, for dilute (decinormal) solutions of caustic potash and hydrochloric acid, the ratio of the velocity-constants K for the saponification of methyl acetate is 1350 : 1. The velocity of saponification by bases also depends upon their electrolytic dissociation. Ammonium hydroxide, for example, being considerably less ionized than caustic potash or caustic soda, saponifies much more slowly than either of these bases. Saponification is therefore caused by the hydroxyl-ion common to all bases.

The velocity of ester-saponification, being proportional to the concentration of the hydrogen ions or hydroxyl-ions, can be employed in determining this concentration. By its aid, the degree of hydrolytic dissociation of potassium cyanide, carbonates of alkali-metals, and other salts can be ascertained, and also the hydrogen-ionization of acid salts, such as potassium hydrogen sulphate, $KHSO_4$.

In the technical saponification of fats with slaked lime (**91**) a much smaller amount of this base is used than would be needed to neutralize all the acid obtained: the saponification is nevertheless complete. This is due to the fact that the higher fatty acids are very weak, so that their salts undergo partial hydrolytic dissociation. Thus, notwithstanding the excess of acid, there is always enough of the free base (hydroxyl-ions) present to effect the saponification.

Esterification of Primary, Secondary, and Tertiary Alcohols.

102. MENSCHUTKIN has investigated the proportions of ester formed when primary, secondary, and tertiary alcohols respectively are heated with an equivalent quantity of acetic acid in sealed tubes for one hour at 154° He has shown that the percentage of ester formed is nearly the same from one member as from another of the same class, while the percentages differ widely for alcohols of different classes. Thus, about 47 per cent. of primary, about 22 per cent. of secondary, and only about 1·5 per cent. of tertiary alcohols are esterified. This difference affords a means of determining to which of the three classes a given alcohol belongs.

IV. Thio-acids, $R\cdot CO\cdot SH$.

103. The *thio-acids* are obtained by the interaction of acid chlorides and potassium hydrogen sulphide, KSH, this method of formation proving their constitution. They are liquids with a most disagreeable odour, and when heated with salts of heavy metals yield a fatty acid and the corresponding metallic sulphide.

V. Acid Amides, $C_nH_{2n+1}\cdot CONH_2$.

104. *Acid amides* are formed by the action of ammonia on acid chlorides or anhydrides, a circumstance which affords a proof of their constitution:

$$C_nH_{2n+1}\cdot CO\boxed{Cl+H}NH_2 = C_nH_{2n+1}\cdot CONH_2+HCl;$$

$$\left.\begin{matrix}C_nH_{2n+1}\cdot CO\\ C_nH_{2n+1}\cdot CO\end{matrix}\right>\boxed{O+\begin{matrix}H\\ H\end{matrix}}\begin{matrix}NH_2\\ NH_2\end{matrix} = 2C_nH_{2n+1}\cdot CONH_2+H_2O.$$

Acid amides are also formed when the ammonium salts of the fatty acids are strongly heated, or when the sodium salts are distilled with ammonium chloride, one molecule of water being eliminated:

$$C_nH_{2n+1}\cdot CO\boxed{O}NH_2\boxed{H_2} = C_nH_{2n+1}\cdot CONH_2+H_2O.$$

When the nitriles are warmed with acids, two molecules of water are taken up, with formation of the corresponding acids (**86**). This reaction can be so modified—for example by dissolving the nitrile in concentrated sulphuric acid—that only one molecule of water is added, when amides are obtained:

$$C_nH_{2n+1}\cdot CN+H_2O = C_nH_{2n+1}\cdot CONH_2.$$

The acid amides are therefore intermediate products in the conversion of nitriles into acids. Distillation with such a dehydrating agent as phosphorus pentoxide converts amides into nitriles by elimination of water, whereas boiling with dilute acids or alkalis produces the corresponding acids by addition of the elements of water.

The acid amides are also formed by the action of ammonia upon esters:

$$CH_3\cdot CO\boxed{OC_2H_5+H}NH_2 = CH_3\cdot CONH_2+C_2H_5OH.$$

The acid amides are solid, crystalline compounds, with the exception of the liquid *formamide*, $\mathrm{H \cdot CONH_2}$. The lower members are soluble in water, and odourless when pure. *Acetamide*, $\mathrm{CH_3 \cdot CONH_2}$, melts at 82°, and distils at 222°. Some specimens have a strong odour suggestive of the excrement of mice, due to slight traces of impurities. The remarkably high boiling-point of this substance is worthy of notice.

The acid amides and the amines greatly differ in their behaviour. Unlike the bond between carbon and nitrogen in the amines, that in the $-\mathrm{C}\Big\langle{}^{\mathrm{O}}_{\mathrm{NH_2}}$-group of the amides is readily severed by boiling with acids or alkalis. Further, the basic properties of ammonia are greatly weakened by the exchange of one of its hydrogen atoms for an acid-radical; and although salts of acid amides do exist, they are decomposed by water. Acetamide hydrochloride, $\mathrm{CH_3 \cdot CO \cdot NH_2 \cdot HCl}$, is such a substance: it is formed by passing dry hydrochloric-acid gas through an ethereal solution of acetamide. The acid amides even possess acidic properties: an aqueous solution of acetamide dissolves mercuric oxide, forming a compound with the formula $\mathrm{(CH_3 \cdot CONH)_2Hg}$.

The behaviour of the amides and amines towards nitrous acid is analogous, the corresponding acids and alcohols respectively being produced by exchange of $\mathrm{NH_2}$ for OH (72).

Amides can be converted into primary amines by a method described in 264.

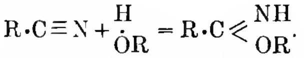
105. Some further derivatives, obtainable from the acids by substitution in the carboxyl-group, are described below.

Amino-chlorides are produced by the action of phosphorus pentachloride on the acid amides:

$$\mathrm{R \cdot CONH_2 + PCl_5 = R \cdot CCl_2 \cdot NH_2 + POCl_3}.$$

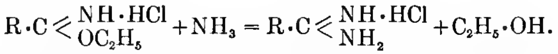
These compounds are only stable when one or both of the hydrogen atoms of the amino-group, $\mathrm{NH_2}$, are replaced by alkyl-radicals. They yield *imino-chlorides*, $\mathrm{R \cdot CCl{:}NH}$, by the elimination of one molecule of HCl, the same compounds being formed by the addition of HCl to nitriles.

Imino-ethers have the constitution $\mathrm{R \cdot C}\Big\langle{}^{\mathrm{NH}}_{\mathrm{OR}}$, and may be regarded as the product of the replacement of the doubly-linked oxygen of the carboxyl-group by the imino-group, NH. They are obtained by combination of alcohols and nitriles under the influence of dry hydrochloric-acid gas:



$$R\cdot C\equiv N+\begin{matrix}H\\ \cdot\\ OR\end{matrix}=R\cdot C\lessgtr\begin{matrix}NH\\OR\end{matrix}.$$

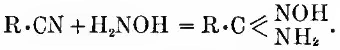
The well-crystallized hydrochlorides of the imino-ethers are converted by treatment with ammonia into the hydrochlorides of the *amidines:*



$$R\cdot C\lessgtr\begin{matrix}NH\cdot HCl\\OC_2H_5\end{matrix}+NH_3=R\cdot C\lessgtr\begin{matrix}NH\cdot HCl\\NH_2\end{matrix}+C_2H_5\cdot OH.$$

The amidines are unstable in the free state, but are strongly monobasic, and form stable salts.

Amidoximes are addition-products of the nitriles and hydroxylamine, NH_2OH:



$$R\cdot CN+H_2NOH=R\cdot C\lessgtr\begin{matrix}NOH\\NH_2\end{matrix}.$$

They yield salts with both acids and bases, and give a flocculent, muddy-brown or green precipitate when treated with an alkaline solution of a copper salt, a reaction which affords a characteristic test for them

Acid hydrazides are produced by the action of hydrazine, $H_2N—NH_2$, on acid chlorides or esters, and therefore have the constitution $R\cdot CONH\cdot NH_2$. Nitrous acid converts them into *acid azides:*

$$R\cdot CONH\cdot NH_2+HNO_2=R\cdot CON_3+2H_2O.$$

The acid azides are volatile, explosive substances, and some yield well-developed crystals.

ALDEHYDES AND KETONES.

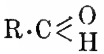
106. Both the aldehydes and ketones have the general formula $C_nH_{2n}O$. They are produced by the oxidation of primary and secondary alcohols respectively. Both classes of alcohols have the general formula $C_nH_{2n+2}O$, so that each oxidation involves the elimination of two hydrogen atoms.

On further oxidation, an aldehyde takes up one oxygen atom, forming the corresponding acid with the same number of carbon atoms; thus $C_nH_{2n}O$ is converted into $C_nH_{2n}O_2$. It follows that an aldehyde is an intermediate product in the oxidation of an alcohol to an acid (49):

$$\underset{\text{Primary alcohol}}{C_nH_{2n+2}O} \rightarrow \underset{\text{Aldehyde}}{C_nH_{2n}O} \rightarrow \underset{\text{Acid}}{C_nH_{2n}O_2}.$$

A primary alcohol has the constitutional formula $C_nH_{2n+1}\cdot CH_2OH$, and on oxidation yields an acid $C_nH_{2n+1}\cdot COOH$. Since in this reaction the alkyl-group, C_nH_{2n+1}, is not altered, it must be present in the aldehyde. Hence, it follows that the two hydrogen atoms removed from the alcohol by oxidation must belong to the group $—CH_2OH$.

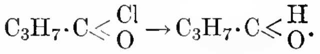
Two structural formulæ are, therefore, possible,



$$R\cdot C\lessgtr^{O}_{H} \quad \text{and} \quad R\cdot C—OH.$$

The improbability of the existence of free bonds or bivalent carbon atoms in compounds (17) constitutes a strong reason against the adoption of the second formula. Moreover, this formula points to the presence in an aldehyde of a hydroxyl-group: in reality, the aldehydes possess none of the properties peculiar to substances containing that group. For example, they do not form esters or ethers, and phosphorus pentachloride does not replace OH by Cl, but effects the exchange of the oxygen atom for two chlorine atoms.

Since the second formula does not represent the properties of the aldehydes, it follows that the first is the correct one. This view is supported by the fact that aldehydes are formed when acid chlorides dissolved in moist ether react with sodium, the chlorine atom being replaced by a hydrogen atom:

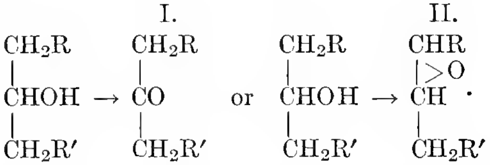


$$C_3H_7\cdot C{<}^{Cl}_{O} \rightarrow C_3H_7\cdot C{<}^{H}_{O}.$$

n-Butyryl chloride *n*-Butyraldehyde

The aldehydes therefore contain the group $—C{<}^{O}_{H}$.

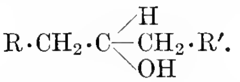
107. Ketones result from the removal by oxidation of two hydrogen atoms from secondary alcohols (**106**). Like the aldehydes, ketones lack the properties peculiar to hydroxyl-compounds, a proof that one of the hydrogen atoms removed comes from the hydroxyl-group. Putting aside the possibility of the formation of free bonds, the second hydrogen atom eliminated must have been attached to the carbon atom linked to oxygen, or to another carbon atom. The two cases are represented below, R and R′ being alkyl-groups:



$$\begin{array}{ccccccc} & & \text{I.} & & & & \text{II.} \\ CH_2R & & CH_2R & & CH_2R & & CHR \\ | & & | & & | & & |{>}O \\ CHOH & \rightarrow & CO & \text{or} & CHOH & \rightarrow & CH \\ | & & | & & | & & | \\ CH_2R' & & CH_2R' & & CH_2R' & & CH_2R' \end{array}\cdot$$

For reasons analogous to those for aldehydes, formula I. is more probable than formula II. The products obtained by the oxidation of ketones indicate that formula I. represents the constitution of this class of compounds.

The general formula for secondary alcohols is



$$R\cdot CH_2\cdot C\begin{array}{l}\diagup H \\ —CH_2\cdot R'. \\ \diagdown OH\end{array}$$

From such an alcohol two acids, $R\cdot CH_2\cdot COOH$ and $R'\cdot CH_2\cdot COOH$, are obtained by strong oxidation, the carbon chain in some of the molecules being severed to the right, and in others to the left, of the CHOH-group. This reaction furnishes a means of identifying the alkyl-radicals attached to the group —CHOH— in a secondary alcohol. Since on oxidation ketones yield the same acids as the corresponding secondary alcohols, the alkyl-groups of the secondary alcohols must remain unchanged in the ketones. Hence, such a structure as that represented by formula II. is excluded, so that formula I. must be correct.

Ketones therefore contain the carbonyl-group CO *in union with two carbon atoms.*

Aldehydes may be looked upon as ketones with an alkyl-group replaced by hydrogen.

Nomenclature.

108. The name aldehyde is derived from *al*(cohol) *dehyd*(rogenatus), that is, "dehydrogenated alcohol." The word ketone has its origin in the name of the first member of the series, *acetone*, $CH_3\cdot CO\cdot CH_3$ (120).

The aldehydes are named after the corresponding acids: *formaldehyde*, $H\cdot CHO$; *acetaldehyde*, $CH_3\cdot CHO$; *propionaldehyde*, $C_2H_5\cdot CHO$; *valeraldehyde*, $C_4H_9\cdot CHO$; etc.

The ketones derive their names from the alkyl-groups which they contain: *dimethylketone*, $CH_3\cdot CO\cdot CH_3$; *methylpropylketone*, $CH_3\cdot CO\cdot C_3H_7$; etc.

Methods of Formation.

109. Several methods besides the oxidation of alcohols are applicable to the preparation of both aldehydes and ketones.

1. Dry distillation of the salts of the fatty acids, calcium acetate yielding acetone:

$$\begin{array}{l|l}\mathrm{CH_3\cdot CO} & \mathrm{O} \\ \mathrm{CH_3\cdot} & \mathrm{COO}\end{array}\!>\mathrm{Ca} = \mathrm{CH_3\cdot CO\cdot CH_3 + CaCO_3}.$$

The conversion of acetic acid and propionic acid into the corresponding ketones is readily effected by passing the vaporized acids over aluminium oxide heated to a temperature above 400°.

When an equivalent quantity of a formate is mixed with the salt of the other fatty acid, an aldehyde is produced by the distillation:

$$\begin{array}{r|l}\mathrm{C_3H_7\cdot CO} & \mathrm{ONa} \\ \mathrm{H} & \mathrm{COONa}\end{array} = \mathrm{C_3H_7\cdot C}\lessdot{}^{\mathrm{O}}_{\mathrm{H}} + \mathrm{Na_2CO_3}.$$

When a mixture of the salts of two different fatty acids, excluding formates, is distilled, *mixed ketones* are obtained:

$$\begin{array}{l} CH_3\cdot CO\boxed{ONa} \\ C_2H_5\cdot\boxed{COONa} \end{array} = \underset{\text{Methylethylketone}}{CH_3\cdot CO\cdot C_2H_5} + Na_2CO_3.$$

In the last two reactions the product contains the corresponding simple ketones in addition to the aldehyde or mixed ketone. Thus, in the foregoing example dimethylketone and diethylketone are also formed.

Given the structure of the fatty acids, the method of formation just described could be adduced as a proof of the constitution of the aldehydes and ketones, if it were not that the reaction only takes place at high temperatures. Since under such conditions organic compounds frequently undergo changes of structure, more especially at the moment of formation, such *pyrogenetic* reactions cannot be regarded as furnishing conclusive evidence of the constitution of a compound.

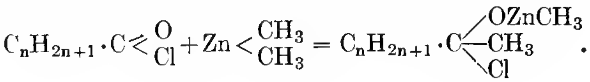
2. Aldehydes or ketones can be obtained from compounds containing two halogen atoms linked to a single carbon atom, by heating them with water:

$$\underset{\text{Ethylidene chloride}}{CH_3\cdot CH\boxed{Cl_2+H_2}O} = CH_3\cdot CHO + 2HCl.$$

3. When primary or secondary alcohols in the gaseous state are passed over finely-divided copper-dust, obtained by reduction of copper oxide, at 250°–400°, they yield hydrogen, and aldehydes or ketones respectively:

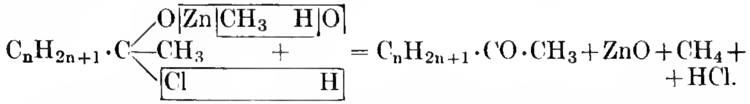
$$C_nH_{2n+1}\cdot OH = H_2 + C_nH_{2n}O.$$

4. An important method for the preparation of ketones, but not of aldehydes, is the interaction of acid chlorides and zinc alkides (82), and subsequent decomposition with water. An addition-product is first formed, its production being due to the transformation of the double bond of the oxygen atom into a single one:



$$C_nH_{2n+1}\cdot C\lessgtr\begin{matrix} O \\ Cl \end{matrix} + Zn<\begin{matrix} CH_3 \\ CH_3 \end{matrix} = C_nH_{2n+1}\cdot C\begin{matrix} \diagup OZnCH_3 \\ -CH_3 \\ \diagdown Cl \end{matrix}.$$

When this addition-product is treated with water a ketone is formed:

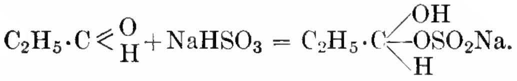


$$C_nH_{2n+1}\cdot C\begin{cases} \boxed{O|Zn|CH_3 \quad H|O} \\ CH_3 \qquad + \\ \boxed{Cl \qquad\quad H} \end{cases} = C_nH_{2n+1}\cdot CO\cdot CH_3+ZnO+CH_4+ +HCl.$$

110. Common to the aldehydes and ketones is the power of forming addition-products. This property is due to the double bond of the oxygen atom, the conversion of which into a single bond sets free a carbon linking and an oxygen linking, and thus enables the aldehydes and ketones to form addition-products with the following elements and compounds.

1. *Hydrogen.*—An addition-product is produced by the action of sodium-amalgam on an aqueous solution of an aldehyde or ketone; or by passing the vapour of the aldehyde or ketone mixed with hydrogen over heated, finely-divided nickel. Primary alcohols are formed from aldehydes, and secondary from ketones.

2. *Sodium hydrogen sulphite.*—When aldehydes or ketones are agitated with a very concentrated aqueous solution of this compound, a crystalline addition-product is obtained:



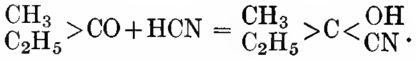
$$C_2H_5\cdot C\Big<\begin{matrix}O\\H\end{matrix}+NaHSO_3 = C_2H_5\cdot C\begin{cases}OH\\OSO_2Na.\\H\end{cases}$$

This constitution is assigned to these compounds because of their ready conversion by the action of dilute acids or sodium-carbonate solution into the corresponding aldehydes or ketones, mere solution in water effecting this decomposition for the higher members. For this reason, it is highly improbable that there is a direct bond between sulphur and carbon (67). The primary sulphite compounds—sometimes incorrectly called "bisulphite" compounds—dissolve readily in water, but are insoluble in very concentrated solutions of the acid sulphite itself.

All ketones do not yield these addition-products. They are most readily obtained from those containing one methyl-group directly linked to carbonyl, or methylketones.

The use of primary sulphite is often exceedingly serviceable for the purification of aldehydes or ketones, or for separating them from reaction-mixtures.

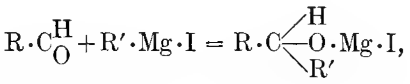
3. *Hydrocyanic acid.*—When an aldehyde or ketone is brought into contact with an aqueous solution of hydrocyanic acid, combination takes place:



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CO+HCN=\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}C{<}\begin{matrix}OH\\CN\end{matrix}.$$

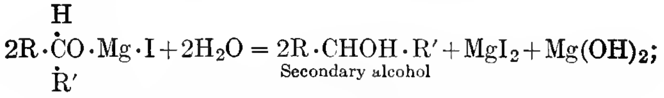
This is an important synthesis, because the *cyanohydrins* or hydroxy-nitriles thus formed can be converted into hydroxy-acids by hydrolysis, a reaction affording a means of synthesizing such compounds (**182**, 5).

111. With GRIGNARD'S alkyl magnesium halides (**82**), aldehydes and ketones form addition-products, and on treatment with water these yield respectively secondary and tertiary alcohols:

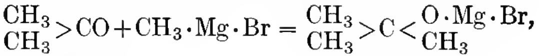


$$R\cdot C\begin{matrix}H\\O\end{matrix}+R'\cdot Mg\cdot I=R\cdot C\begin{matrix}\diagup H\\—O\cdot Mg\cdot I,\\\diagdown R'\end{matrix}$$

Aldehyde Addition-product

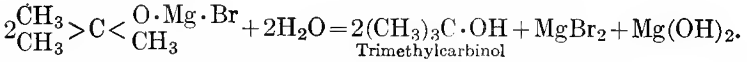


$$2R\cdot\overset{H}{\underset{R'}{C}}O\cdot Mg\cdot I+2H_2O=\underset{\text{Secondary alcohol}}{2R\cdot CHOH\cdot R'}+MgI_2+Mg(OH)_2;$$



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CO+CH_3\cdot Mg\cdot Br=\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}\begin{matrix}O\cdot Mg\cdot Br,\\CH_3\end{matrix}$$

Acetone Addition-product



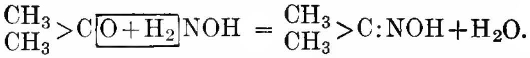
$$2\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}\begin{matrix}O\cdot Mg\cdot Br\\CH_3\end{matrix}+2H_2O=2(CH_3)_3C\cdot OH+MgBr_2+Mg(OH)_2.$$

Trimethylcarbinol

112. Other reactions common to aldehydes and ketones depend upon exchange of the doubly-linked oxygen atom for other atoms or groups.

1. *Phosphorus pentachloride* replaces the oxygen atom by two chlorine atoms.

2. *Hydroxylamine* reacts in accordance with the equation



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C\boxed{O+H_2}NOH=\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{:}NOH+H_2O.$$

Oximes are thus produced, and are called *aldoximes* when derived from aldehydes, and *ketoximes* when derived from ketones. This reaction is of very general application. The oximes are either crystalline compounds, or liquids, and possess both acidic and basic properties. When they are treated with bases, the hydrogen of the hydroxyl-group is replaced by a metal; with acids, addition-products are formed, the reaction being similar to the production of ammonium salts:

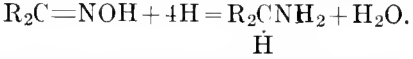
$$(CH_3)_2C{=}NOH\cdot HCl.$$

Acetoxime hydrochloride

On boiling with dilute hydrochloric acid, the oximes take up one molecule of water, yielding hydroxylamine, and either an aldehyde or a ketone.

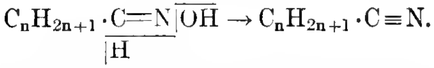
The constitution of the oximes is discussed in 257.

Energetic reduction converts the oximes into amines:



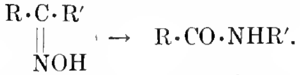
$$R_2C{=}NOH + 4H = R_2\underset{H}{\overset{\cdot}{C}}NH_2 + H_2O.$$

The aldoximes are readily transformed into the corresponding nitriles by the action of dehydrating agents, such as acetic anhydride:



$$C_nH_{2n+1}\cdot\underset{|H}{C}{=}N|\overline{OH} \rightarrow C_nH_{2n+1}\cdot C\equiv N.$$

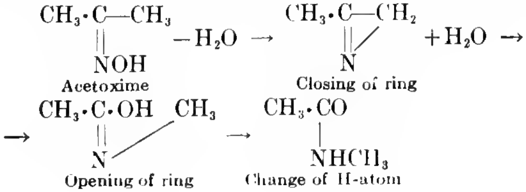
Ketoximes undergo a remarkable rearrangement of the atoms in the molecule or *intramolecular transformation,* called after its discoverer the "BECKMANN transformation." It takes place, for example, under the influence of acetyl chloride. The ketoximes thus yield acid amides, with substituents in union with the nitrogen atom.



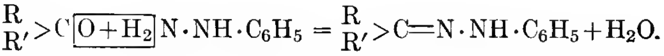
$$\begin{array}{c} R\cdot C\cdot R' \\ \| \\ NOH \end{array} \rightarrow R\cdot CO\cdot NHR'.$$

Oxime Amide

WALLACH regards this reaction as resulting from the formation of a closed chain of three atoms by union at one point, followed by the opening of the ring at another point. The formation of methylacetamide from acetoxime is represented by the scheme



The behaviour of aldehydes and ketones with *phenylhydrazine*, $C_6H_5NH\cdot NH_2$ (**344**), is exactly analogous to that with hydroxylamine:



$$\begin{matrix}R\\R'\end{matrix}\!>C\boxed{O+H_2}N\cdot NH\cdot C_6H_5 = \begin{matrix}R\\R'\end{matrix}\!>C{=}N\cdot NH\cdot C_6H_5+H_2O.$$

Phenylhydrazine Phenylhydrazone

The substances formed, called *hydrazones*, are either well-defined crystalline compounds, or liquids. When heated with hydrochloric acid, they take up the elements of water, forming phenylhydrazine and the corresponding aldehyde or ketone. Phenylhydrazine and hydroxylamine are important reagents for detecting the presence of the carbonyl-group.

The constitution of the phenylhydrazones is thus established. Derivatives of phenylhydrazine obtained by replacement of the hydrogen of the imino-group, —NH, by an alkyl-group, react with aldehydes and ketones similarly to phenylhydrazine itself, so that the structure $R_2C<\begin{array}{l}NH\\ \vdots\\ N\cdot C_6H_5\end{array}$ is excluded. This is rendered even more evident by the fact that only phenylhydrazines containing an unsubstituted amino-group can form hydrazones.

ALDEHYDES.

113. In addition to the properties common to both aldehydes and ketones (**110** to **112**), aldehydes have their own special properties.

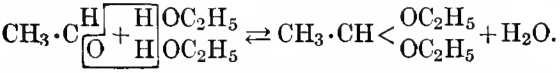
1. *Aldehydeammonia.*—Acetaldehydeammonia is produced from ammonia and acetaldehyde:

$$\underset{\text{Acetaldehyde}}{C_2H_4O}+NH_3 = \underset{\text{Acetaldehydeammonia}}{C_2H_4ONH_3}.$$

It is precipitated in the form of white crystals when dry ammonia-gas is passed into a solution of acetaldehyde in anhydrous ether, and is very soluble in water. Acids decompose the aldehyde-ammonias into an aldehyde and ammonia; caustic potash is unable to effect this decomposition.

At ordinary temperatures the molecular formula of acetaldehyde-ammonia is three times its empirical formula. When dried over sulphuric acid, it loses water and is converted into $(CH_3\cdot CHNH)_3$, (114) a polymeride of ethylidene-imine.

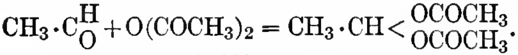
2. *Acetals.*—An aldehyde combines with two molecules of an alcohol, with elimination of water, and production of an *acetal:*



$$\mathrm{CH_3\cdot C}\begin{array}{l}\mathrm{H}\\ \mathrm{O}\end{array}+\begin{array}{l}\mathrm{H}\,|\,\mathrm{OC_2H_5}\\ \mathrm{H}\,|\,\mathrm{OC_2H_5}\end{array}\rightleftarrows \mathrm{CH_3\cdot CH}<\begin{array}{l}\mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\end{array}+\mathrm{H_2O}.$$

Acetals are readily obtained by addition of the aldehyde to a one per cent. solution of anhydrous hydrochloric acid in the alcohol. The reaction is not complete; it is limited by the reverse one, since water acts on acetal, regenerating aldehyde and alcohol. Both the formation and decomposition of acetal are considerably accelerated by the presence of a small quantity of a strong mineral acid, which acts as a powerful catalyst. The acetals are liquids of aromatic odour, and distil without decomposition. They are not attacked by alkalis, but are resolved by acids into the compounds from which they were produced, a fact which supports the view expressed in the above structural formula, that the alkyl-groups and the aldehyde-residue are indirectly united by oxygen, the stability of a carbon chain being sufficient to resist the action of such reagents.

3. *Reaction with acid anhydrides.*—Addition-products are obtained with acid anhydrides:



$$\mathrm{CH_3\cdot C}\begin{array}{l}\mathrm{H}\\ \mathrm{O}\end{array}+\underset{\text{Acetic anhydride}}{\mathrm{O(COCH_3)_2}}=\mathrm{CH_3\cdot CH}<\begin{array}{l}\mathrm{OCOCH_3}\\ \mathrm{OCOCH_3}\end{array}.$$

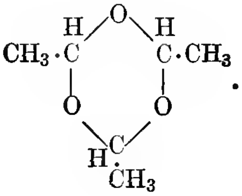
Acetic anhydride

These compounds are analogous to the acetals. They are easily decomposed by water, and still more readily by alkalis, into the corresponding acid and aldehyde.

114. Two kinds of addition-products are also formed by the union of aldehyde molecules with one another. When a few drops of concentrated sulphuric acid are added to acetaldehyde, a liquid boiling at 22°, the mixture becomes warm, and then begins to boil violently. At the end of the reaction a colourless liquid is obtained, similar to the original one, but boiling about 100° higher, at 124°. The empirical formula of this compound is the same as that of acetaldehyde, C_2H_4O, but its vapour-density is three times as great, so that it has the molecular formula $C_6H_{12}O_3$. This substance, *paracetaldehyde*, is readily converted into acetaldehyde by distillation with dilute sulphuric acid, another example of a reaction limited by the reverse one:

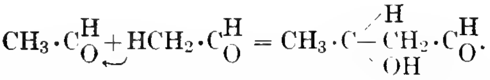
$$C_6H_{12}O_3 \rightleftarrows 3C_2H_4O.$$

The equilibrium reached must be independent of the nature of the acid, that is, of the catalyst ("Inorganic Chemistry," 49), as has been proved for this reaction by experiment. The same equilibrium must be attained without the aid of any catalyst, but the change proceeds so slowly that no experimental proof has yet been possible. A direct union between the carbon atoms of the three aldehyde molecules in paracetaldehyde is improbable, and the existence of an indirect linking through the oxygen atoms must be assumed, because it accounts for the ease with which the molecule of paracetaldehyde can be resolved. The compound is not attacked by sodium, and therefore cannot contain hydroxyl-groups. It lacks all the characteristics of aldehydes, proving the absence of the group $—C{<}^{O}_{H}$. These properties are best expressed by the constitutional formula



The union of two or more molecules of a substance to form a body from which the original compound can be regenerated is called *polymerization.*

115. Under the influence of dilute alkali-solutions aldehyde molecules combine with production of compounds of a different kind. When an aqueous solution of acetaldehyde is warmed with concentrated caustic potash, the liquid becomes yellow; after a short time, reddish-yellow, amorphous masses are precipitated. The aldehyde has *resinified*, and the reddish-yellow substance formed is called *aldehyde-resin*. When, however, dilute caustic potash (or sodium acetate, zinc chloride, etc.) is added to acetaldehyde, a substance is formed having the same empirical composition as acetaldehyde, but with double the molecular formula, $C_4H_8O_2$. This compound is called *aldol:* it is a liquid, distilling without decomposition under diminished pressure, and readily undergoing polymerization. It possesses the properties characteristic of aldehydes, yielding on oxidation, for example, an acid with the same number of carbon atoms. The acid thus obtained has the formula $C_4H_8O_3$, and is a n-hydroxybutyric acid; that is, n-butyric acid with one H-atom of the alkyl-group replaced by hydroxyl. It can be converted into n-butyric acid, with a chain of four carbon atoms, proving the presence of a similar chain in aldol. Hence, in this case, the union of the aldehyde molecules has been effected through the carbon bonds, a view supported by the fact that aldol cannot be reconverted into aldehyde. The combination of the aldehyde molecules to form aldol may be represented by the equation

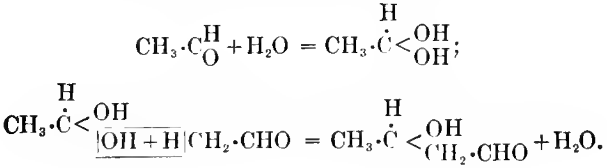


$$CH_3\cdot C{\genfrac{}{}{0pt}{}{H}{O}} + HCH_2\cdot C{\genfrac{}{}{0pt}{}{H}{O}} = CH_3\cdot \overset{H}{\underset{OH}{C}}-CH_2\cdot C{\genfrac{}{}{0pt}{}{H}{O}}.$$

Aldol

This constitutional formula expresses the properties of aldol.

Instead of explaining the formation of aldol by assuming the combination of one of the hydrogen atoms of one aldehyde molecule with the oxygen atom of another to form hydroxyl, it might be supposed that an aldehyde molecule unites with a molecule of water, the addition-product formed reacting with a second molecule of aldehyde with elimination of water:



$$CH_3\cdot C{\genfrac{}{}{0pt}{}{H}{O}} + H_2O = CH_3\cdot \overset{H}{\dot{C}}<{\genfrac{}{}{0pt}{}{OH}{OH}};$$

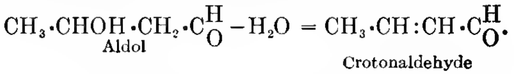
$$CH_3\cdot \overset{H}{\dot{C}}<{\genfrac{}{}{0pt}{}{OH}{\underline{|OH+H|}CH_2\cdot CHO}} = CH_3\cdot \overset{H}{\dot{C}}<{\genfrac{}{}{0pt}{}{OH}{CH_2\cdot CHO}}+H_2O.$$

Aldol

Reactions are often explained by assuming the formation of such addition-products and the subsequent elimination of water. In a few instances this view has been experimentally verified.

Aldol is both an alcohol and an aldehyde, hence its name, *ald*(ehyde-alcoh)*ol*. The union of molecules through carbon bonds, as in the formation of aldol, with the production of compounds from which the original substance cannot be regenerated by any simple method, is called *condensation*.

It is probable that aldehyde-resin is a product resulting from continued condensation of the aldol molecules with elimination of water, just as aldol itself readily loses one molecule of water when heated, with formation of crotonaldehyde (148):



$$\underset{\text{Aldol}}{CH_3\cdot CHOH\cdot CH_2\cdot C\genfrac{}{}{0pt}{}{H}{O}} - H_2O = \underset{\text{Crotonaldehyde}}{CH_3\cdot CH{:}CH\cdot C\genfrac{}{}{0pt}{}{H}{O}}.$$

Tests for Aldehydes.

116. The following tests serve for the detection of aldehydes.

1. Resinification with alkalis.

2. Reduction of an ammoniacal silver solution. This solution is prepared by adding excess of caustic potash to a solution of silver nitrate, and then just sufficient ammonia to dissolve the precipitated silver oxide. When this liquid is brought into a dilute aqueous solution of an aldehyde, and the mixture warmed, a beautiful mirror of metallic silver is deposited on the sides of the tube.

3. When an aldehyde is added to a solution of magenta decolorized by sulphurous acid—SCHIFF'S reagent—the red colour is restored.

Formaldehyde, $H\cdot C{<}\genfrac{}{}{0pt}{}{H}{O}$.

117. Formic acid, the first member of the homologous series of fatty acids, has certain properties not possessed by the higher members (88). *Formaldehyde* affords another striking example of this phenomenon of disparity between the first and succeeding members in a homologous series.

It is obtained by the oxidation of methyl alcohol, effected by passing a mixture of air and methyl-alcohol vapour over a hot spiral of platinum or copper. The heat produced by the reaction is sufficient to raise the temperature of the spiral to redness, and to maintain it at that point, provided the stream of gas is passed over it with sufficient velocity. The formaldehyde produced is absorbed by water, in which it dissolves readily.

This aldehyde is a product of the incomplete combustion of wood, peat, and many other organic substances. This fact explains its presence in traces in the atmosphere, especially in that of large towns.

Formaldehyde has a very pungent odour. At ordinary temperatures it is gaseous, but when cooled with solid carbon dioxide and ether, it forms a liquid boiling at —20° Even at this temperature polymerization begins, and at higher temperatures it proceeds with explosive energy. When the aqueous solution is evaporated, *paraformaldehyde*, a crystalline polymeride of unknown molecular weight, is produced. It melts at 63° On concentrating a solution of formaldehyde with strong sulphuric acid, only part of the formaldehyde is evolved as gas; the rest polymerizes, and remains as a white, crystalline mass, a mixture of α-, β-, and γ-*polyoxymethylene*. The molecular weights of these polymerides are not known: on heating, they are reconverted into formaldehyde, proving them true polymerides. Prolonged heating of the γ-variety with water yields another polymeride, δ-*polyoxymethylene*. On treatment with ammonia at the ordinary temperature, formaldehyde does not yield an aldehydeammonia, but a complicated compound, $C_6H_{12}N_4$, *hexamethylenetetramine*, $(CH_2)_6N_4$, a crystalline, basic substance. At 120°–160° and increased pressure, methylamines are formed:

$$3NH_3+3CH_2O=2NH_2\cdot CH_3+CO_2+H_2O;$$

$$2NH_3+6CH_2O=2NH(CH_3)_2+2CO_2+2H_2O;$$

$$2NH_3+9CH_2O=2N(CH_3)_3+3CO_2+3H_2O.$$

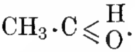
When treated with caustic potash, formaldehyde does not resinify, but is converted into methyl alcohol and formic acid:

$$2CH_2O + H_2O = CH_3OH + HCOOH.$$

The oxime of formaldehyde also polymerizes readily. Formaldehyde and its derivatives display a much greater tendency towards polymerization than the other aldehydes and their derivatives, and differ from them in their behaviour with ammonia and with caustic potash.

An aqueous solution containing 40 per cent. of formaldehyde is a commercial product, and is called "formalin." After dilution, it is employed as a disinfectant, and in the preservation of anatomical specimens. It possesses the remarkable property of converting proteïn substances into a hard, elastic mass, quite insoluble in water. The contents of a hen's egg, for example, undergo this transformation through contact with formalin for half-an-hour; brain-substance attains the consistency of india-rubber; and a solution of gelatin is converted into a hard, transparent, insoluble, odourless mass, reducible to a fine powder. Before development, photographic films with a basis of gelatin are immersed in a dilute solution of formaldehyde for a short time to render the gelatin insoluble.

The concentration of a formalin solution is determined by adding excess of a solution of twice normal sodium hydroxide, and then hydrogen peroxide, the formaldehyde being converted completely into formic acid. The excess of alkali is estimated by titration, and from the result the amount of formaldehyde can be calculated, since one molecule of the aldehyde yields one molecule of the acid.



Acetaldehyde, $CH_3\cdot C\lessgtr^{H}_{O}$.

118. *Acetaldehyde* is the typical aldehyde of this series, since it has all the properties characteristic of aldehydes as a class. It is obtained by the oxidation of ethyl alcohol by means of potassium dichromate and sulphuric acid, and is a liquid with a disagreeable odour, at least in the dilute state: it boils at 22°, and solidifies at $-120\cdot6°$. It readily polymerizes to paracetaldehyde, $C_6H_{12}O_3$ (114).

Acetaldehyde is only partially converted into paracetaldehyde by dilute sulphuric acid, an equilibrium being attained:

$$3C_2H_4O \rightleftarrows C_6H_{12}O_3.$$

Although this equilibrium would also result in absence of the catalyst—sulphuric acid,—it has been proved by experiment that at temperatures below 130° the transformation is then so slow as to produce no appreciable change in the relative proportion of acetaldehyde and its polymeride in a mixture, even after the lapse of a long period of time. Acetaldehyde and paracetaldehyde can be readily obtained from such a mixture, there being a difference of about 100° between their boiling-points.

The relationship between acetaldehyde and paracetaldehyde is graphically represented in Fig. 31, in which the curve *FHG* gives the boiling-points of mixtures of the two substances in varying proportion. It is plotted by heating to their boiling-points mixtures of the two isomerides, in known proportion, under a reflux-condenser, and noting the temperature. Thus, the point *H* represents a mixture containing 53·5 per cent. of paracetaldehyde, and boiling at 41°.

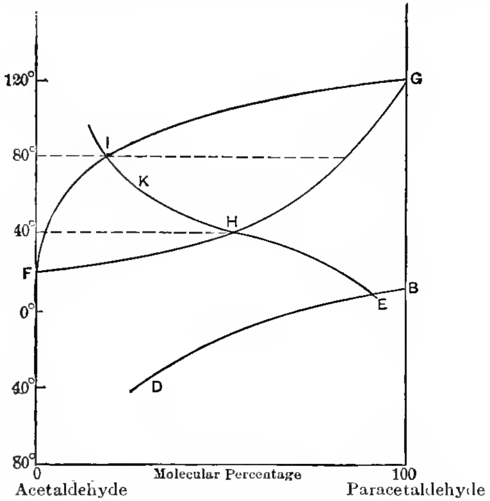


FIG. 31.—RELATIONSHIP BETWEEN ACETALDEHYDE AND PARACETALDEHYDE.

The composition of the vapour—that is, of the first portion of the distillate—yielded by the mixture of the two substances is given by the curve *FIG*. It should be noted that the quantity distilled is small relative to that of the residual mixture, so that the composition of the latter undergoes no appreciable alteration. To ascertain the composition of a mixture boiling at 80°, and of the corresponding vapour, it is only necessary to draw a horizontal line through the point 80° on the ordinate. The point of intersection of this line and the curve *FHG* gives the composition of the mixture, and its intersection with *FIG* that of its vapour.

The curve *DEB* forms part of the cryoscopic curve of paracetaldehyde, when mixed with increasing quantities of acetaldehyde. In accordance with the rule, the freezing-point of the pure substance—paracetaldehyde—is lowered by admixture with a foreign substance—acetaldehyde.

These statements hold for mixtures of the two substances in absence of a catalyst. When this is present, the conditions are wholly different. At any given temperature a mixture of definite composition is speedily formed, both when one of the pure substances and the catalyst alone were present, and when an arbitrary mixture of the two substances in presence of the catalyst constituted the starting-point. There is, therefore, a definite equilibrium corresponding with each temperature, the equilibriums being graphically represented by the curve *KHE*. At 41·7° it intersects the boiling-point curve at the point *H*, indicating that when a mixture of the two substances in arbitrary proportions is heated with a catalyst, its boiling-point changes until it finally boils constantly at 41·7° The mixture boiling at this temperature contains 53·5 per cent. of paracetaldehyde, and 46·5 per cent. of acetaldehyde. The resulting vapour, however, contains 97·5 per cent. of acetaldehyde, as is indicated by the intersection of the horizontal line with the curve *FIG* at the point *I*. This explains the long-established fact that almost pure acetaldehyde is obtained by distilling paracetaldehyde with a small quanity of sulphuric acid.

The equilibrium-curve intersects the cryoscopic curve at *E*, this point corresponding with the temperature 6·8°, and 88·1 per cent. of paracetaldehyde. It follows that a mixture in any proportion should freeze in presence of a catalyst at 6·8°, with separation of pure paracetaldehyde, and that either of the two pure substances must behave similarly on addition of a trace of sulphuric acid.

Another polymeride of acetaldehyde is called *metacetaldehyde:* it is a crystalline product, its polymeric character being inferred from its reconversion into acetaldehyde by heat. It begins to sublime at 150°. Like paracetaldehyde, it does not answer to the ordinary aldehyde-tests; thus, it is not resinified by alkalis. Metacetaldehyde has probably a higher molecular weight than paracetaldehyde. The direct transformation of one into the other is not feasible.

KETONES.

119. The properties characteristic of the ketones are described in **110** to **112**. The first member of the homologous series cannot contain less than three carbon atoms.

Ketones have the general formula $R\cdot CO\cdot R'$, and are always divided at the carbonyl-group by oxidation (**107**); that is, oxidation occurs at that part of the molecule already containing oxygen (**49**). The decomposition can, however, take place in two different ways:

$$R\cdot\underset{\text{I}}{|}CO\cdot R' \quad \text{or} \quad R\cdot CO\cdot\underset{\text{II}}{|}R'.$$

Thus, methylnonylketone, $CH_3\cdot\underset{\text{I}}{|}CO\cdot\underset{\text{II}}{|}C_9H_{19}$, can yield formic acid, CH_2O_2, and capric acid, $C_{10}H_{20}O_2$; or acetic acid, $C_2H_4O_2$, and pelargonic acid, $C_9H_{18}O_2$; the decomposition taking place at the points indicated by the lines I. and II. respectively. The oxidation is such that the decomposition takes place at both points simultaneously, so that four acids are obtained. Two of them may be identical; for example, the oxidation of methylethylketone, $CH_3\cdot CO\cdot C_2H_5$, produces acetic acid and acetic acid by decomposition at point II., and formic acid and propionic acid by decomposition at I. Usually the reaction which leaves the carbonyl in union with the smallest alkyl-residue predominates. Oxidation therefore affords a means of determining the position of the carbonyl-group in the ketone molecule.

The ketones are further distinguished from the aldehydes by their behaviour towards ammonia: this reaction has been carefully investigated for acetone, the first member of the series. By elimination of water it yields complicated substances, such as *diacetoneamine*, $C_6H_{13}NO$ or $(2C_3H_6O+NH_3-H_2O)$, *triacetoneamine*, $C_9H_{17}NO$ or $(3C_3H_6O+NH_3-2H_2O)$, and so on.

The ketones do not yield polymerides, but are capable of forming condensation-products.

Acetone, $CH_3\cdot CO\cdot CH_3$.

120. Acetone is prepared on the manufacturing scale from crude wood-spirit (**46**), and by the dry distillation of calcium acetate. It is present in very small quantities in normal urine, but in much greater proportion in pathological cases, such as *diabetes mellitus* and *acetonuria.* It is a liquid of peculiar, peppermint-like odour, boils at 56·3°, solidifies at −94·9°, and has a specific gravity of 0·812 at 0°. It is an excellent solvent for many organic compounds, and is miscible in all proportions with water. It is converted by reduction into *iso*propyl alcohol (156), and yields a crystalline oxime melting at 69°.

Sulphonal, an important soporific, is prepared from acetone. In presence of hydrochloric acid, acetone unites with ethylmercaptan with elimination of water:

$$(CH_3)_2CO + 2HS{\cdot}C_2H_5 = \underset{\substack{\text{Dimethyldiethyl-}\\\text{mercaptole}}}{(CH_3)_2C(SC_2H_5)_2} + H_2O.$$

Oxidation with potassium permanganate converts the two sulphur atoms of this compound into SO_2-groups, forming diethylsulphonedimethylmethane, $(CH_3)_2C(SO_2C_2H_5)_2$, or sulphonal. It crystallizes in colourless prisms, soluble with difficulty in cold water, and melting at 126°.

Thioaldehydes and Thioketones.

121. In the *thioaldehydes* and *thioketones* sulphur has replaced oxygen. Thioacetaldehyde is not known, but its polymeride. *trithioacetaldehyde,* $C_3H_{12}S_3$, is obtained by passing sulphuretted hydrogen through a mixture of acetaldehyde and hydrochloric acid, Oxidation converts it into a trisulphone (67), each sulphur atom being oxidized to an SO_2-group.

Although acetone itself does not polymerize, replacement of its oxygen atom by a sulphur atom confers this property on it in a high degree. The polymerization of *thioacetone* can be effected by the methods employed for aldehydes. Three molecules become united, forming *trithioacetone,* $C_9H_{18}S_3$.

UNSATURATED HYDROCARBONS.

I. ALKYLENES OR OLEFINES, C_nH_{2n}.

Methods of Formation.

122. 1. The *olefines* are formed in the dry distillation of complicated carbon compounds, a fact which accounts for their presence to the extent of 4–5 per cent. in coal-gas.

2. By elimination of the elements of water from the alcohols $C_nH_{2n+2}O$:

$$C_5H_{11}\cdot OH = C_5H_{10} + H_2O.$$

This can sometimes be effected by heat alone, as with tertiary alcohols, but it is usually necessary to warm the alcohol with a dehydrating agent, such as concentrated sulphuric acid (**60** and **125**) or zinc chloride. Water is more readily eliminated from the secondary and tertiary alcohols than from the corresponding primary compounds.

3. By abstraction of hydrogen halide from alkyl halides, effected by heating with alcoholic potash, a solution of caustic potash in alcohol:

$$C_nH_{2n+1}I + KOC_2H_5 = C_nH_{2n} + KI + C_2H_5OH.$$

An ether is also formed (**61**):

$$C_nH_{2n+1}I + KOC_2H_5 = C_nH_{2n+1}OC_2H_5 + KI.$$

With alkyl iodides the reaction chiefly follows the first equation, the secondary and tertiary iodides being specially adapted for the production of unsaturated hydrocarbons.

Name.	Formula.	Boiling-point.	Name.	Formula.	Boiling-point.
Ethylene. . . .	C_2H_4	−103°	Heptylene . .	C_7H_{14}	98°
Propylene. .	C_3H_6	−180°	Octylene. . . .	C_8H_{16}	124°
n-Butylene. .	C_4H_8	− 5°	Nonylene. . .	C_9H_{18}	153°
n-Amylene. . .	C_5H_{10}	35°	Decylene. . . .	$C_{10}H_{20}$	172°
Hexylene. . .	C_6H_{12}	68°	Undecylene.	$C_{11}H_{22}$	195°

The names of the members of this series are derived from those of the saturated hydrocarbons by altering the termination "ane" to "ylene." These compounds are denoted by the general name *alkylenes* or *olefines*.

To indicate the position of the double bond in the molecule, the alkylenes are sometimes regarded as substituted ethylenes: thus, $CH_3 \cdot CH:CH \cdot CH_3$ is called *symmetrical dimethylethylene;* and $(CH_3)_2C:CH_2$, *unsymmetrical dimethylethylene.*

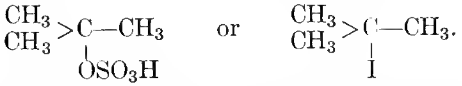
Properties.

123. The lowest members of this homologous series are gases, and are slightly soluble in water: the higher members are liquids or solids, insoluble in water, but soluble in alcohol and ether. At their melting-points the specific gravities of the lower members are about 0·63, rising with increase in the number of carbon atoms to about 0·79.

Their most important chemical property is the power of forming addition-products, and on account of it they are said to be *unsaturated.* Addition-products are very readily obtained by the action of the halogens, especially bromine, on the olefines and other substances containing a double bond, the presence of which can be detected by the decolorization of bromine-water. Another test for the presence of a double bond, suggested by von Baeyer, is carried out by agitating the substance with a dilute solution of potassium permanganate and sodium carbonate. Owing to the reducing action of compounds containing a double carbon bond, the violet colour of the permanganate quickly disappears, with formation of a brown-red, flocculent precipitate of hydrated manganese dioxide. Compounds of other classes, such as aldehydes, react similarly with potassium permanganate, so that the test can only be applied in their absence to hydrocarbons, unsaturated acids, and a few other substances.

The hydrogen halides react by addition with the olefines to form the alkyl halides, hydriodic acid combining very readily.

Concentrated sulphuric acid yields the alkylsulphuric acids by addition: it is sometimes necessary to employ the fuming acid. The addition of sulphuric acid, like that of the hydrogen halides, results in the union of the acid-residue with the unsaturated carbon atom linked to the smallest amount of hydrogen. For example, *iso*butylene, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{:}CH_2$, treated with sulphuric or hydriodic acid yields



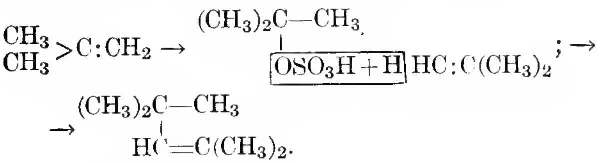
$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}\underset{\displaystyle OSO_3H}{\underset{|}{C}}{-}CH_3 \quad \text{or} \quad \begin{matrix}CH_3\\CH_3\end{matrix}{>}\underset{\displaystyle I}{\underset{|}{C}}{-}CH_3.$$

This reaction may be otherwise expressed by stating that there is a tendency for the number of methyl-groups to increase in such addition-reactions.

Hypochlorous acid, Cl·OH, can also form addition-products which are chloro-alcohols:

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + Cl\cdot OH = \underset{\text{Glycolchlorohydrin}}{CH_2Cl\cdot CH_2OH}.$$

124. Olefines can form condensation-products, butylene and the amylenes yielding them on treatment with moderately dilute sulphuric acid, although ethylene cannot be similarly condensed. The condensation may be explained by assuming that an addition-product with sulphuric acid, or alkylsulphuric acid, is first formed, and then reacts with a second molecule of the olefine:



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{:}CH_2 \rightarrow \begin{matrix}(CH_3)_2C{-}CH_3\\ |\\ \boxed{OSO_3H+H}\,HC{:}C(CH_3)_2\end{matrix}; \rightarrow$$
$$\rightarrow \begin{matrix}(CH_3)_2C{-}CH_3\\ |\\ HC{=}C(CH_3)_2.\end{matrix}$$

The simplest member of this series, CH_2, *methylene*, has not been obtained. Various attempts have been made to prepare it: for instance, by the elimination of HCl from methyl chloride. Such experiments have always resulted in the formation, not of methylene, but of ethylene, two CH_2-groups uniting to form a single molecule.

Ethylene, C_2H_4.

125. Ethylene is a gas, and is usually prepared by heating a mixture of ethyl alcohol and sulphuric acid. Ethylsulphuric acid is first formed (**60**), and on further heating decomposes into ethylene and sulphuric acid:

$$C_2H_5SO_4H = C_2H_4 + H_2SO_4.$$

In the preparation of ether (**62**) the temperature is maintained below a certain limit, and fresh alcohol is continually added, but in this reaction a higher temperature is employed, and no alcohol is added. At the temperature of the reaction, sulphur dioxide and carbon dioxide are produced, but can be removed from the ethylene by passing it through dilute alkali. A purer product is obtained by passing the vapour of ethyl alcohol over clay balls heated at 300°–400°, water and ethylene being formed. When passed over aluminium oxide at 400°, ether-vapour also gives a good yield of water and ethylene.

Ethylene can also be prepared from ethylene bromide, $C_2H_4Br_2$, by removal of its two bromine atoms, which is effected by bringing it into contact with a copper-zinc couple.

Ethylene possesses a peculiar, sweetish odour, and burns with a luminous flame. It is slightly soluble in water and in alcohol. When passed into bromine it is quickly converted into ethylene bromide, $C_2H_4Br_2$ (**154**). It is readily absorbed by concentrated sulphuric acid at 170°, with formation of ethylsulphuric acid. SABATIER found that a mixture of hydrogen and ethylene is changed completely into ethane when passed over finely-divided nickel at temperatures of less than 300° (**29**).

Amylenes, C_5H_{10}.

126. A mixture of isomeric amylenes and pentane is technically prepared by heating fusel-oil (**47**) with zinc chloride.

The isomeric amylenes can be separated by two methods, also applicable in other similar cases. One is based on the solubility at a low temperature of some of the isomerides in a mixture of equal volumes of water and concentrated sulphuric acid, with formation of amylsulphuric acids; the other isomerides are insoluble. This treatment, however, converts part of the amylenes into condensation-products, called *diamylene* and *triamylene*. The other mode of separation depends upon the different velocities with which the isomeric amylenes form addition-products with hydriodic acid.

The Nature of the Double Carbon Bond.

127. Hitherto the existence of a double carbon bond in the alkylenes has been arbitrarily assumed: the constitution of unsaturated compounds could, however, be represented in a variety of ways.

1. *Existence of bivalent or tervalent carbon atoms:*

$$CH_3—\overset{II}{C}—CH_3, \qquad \overset{III}{CH_2}—\overset{III}{CH}—CH_3.$$

2. *Existence of free bonds:*

a. On one carbon atom only:

$$CH_3—\underset{\wedge}{C}—CH_3.$$

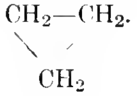
b. On different carbon atoms:

$$CH_3—\underset{|}{CH}—\underset{|}{CH_2}.$$

3. *Existence of a double carbon bond:*

$$CH_3—CH{=}CH_2.$$

4. *Existence of a closed chain or ring:*

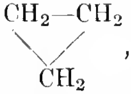


It is stated in **123** that unsaturated compounds are convertible into saturated compounds by addition of atoms or groups. The constitution of these addition-products on the one hand, and the method of formation of the unsaturated products obtained by the elimination of a hydrogen halide, etc., from the saturated compounds on the other, enable a decision to be arrived at between these four possibilities.

It should be observed that the addition-product is the same, whether the existence of a bivalent carbon atom, or of two free bonds on the same carbon atom, be assumed. Thus, whether propylene be supposed to have the constitution $CH_3 \cdot \overset{II}{C} \cdot CH_3$ or $CH_3 \cdot \underset{\wedge}{C} \cdot CH_3$, the addition of bromine produces the same substance, $CH_3 \cdot CBr_2 \cdot CH_3$. Similarly, the assumption of tervalent carbon atoms, or of free bonds on different carbon atoms, leads to the same result; $\overset{III}{C}H_2 \cdot \overset{III}{C}H_2$ with two tervalent carbon atoms, and $\underset{|}{C}H_2 \cdot \underset{|}{C}H_2$ with free bonds, yielding with bromine the same addition-product, $CH_2Br \cdot CH_2Br$. It follows that for the present it is unnecessary to treat cases 1 and 2 separately.

It is readily proved that addition does not take place at only one carbon of unsaturated compounds, for otherwise ethylene chloride, $C_2H_4Cl_2$, would have the constitution $CH_3 \cdot CHCl_2$, and ethylene itself, $CH_3 \cdot CH$. Ethylene chloride would then be identical with the product obtained by the action of phosphorus pentachloride upon acetaldehyde, $CH_3 \cdot CHO$, since the exchange of the oxygen atom in the latter for two chlorine atoms yields a compound of the formula $CH_3 \cdot CHCl_2$. But ethylene chloride is different from the compound $C_2H_4Cl_2$ (*ethylidene chloride*) got from aldehyde. Similarly, propylene chloride, $C_3H_6Cl_2$, formed by the addition of chlorine to propylene, is not identical with the reaction-product obtained by treating acetone with phosphorus pentachloride, $CH_3 \cdot CCl_2 \cdot CH_3$ (*chloroacetone*), nor with that from propionaldehyde, $CH_3 \cdot CH_2 \cdot CHCl_2$ (*propylidene chloride*). Ethylene therefore cannot have either the formula $CH_3 \cdot \underset{\wedge}{C}H$ or $CH_3 \cdot \overset{II}{C}H$, nor propylene any of the formulæ $CH_3 \cdot \underset{\wedge}{C} \cdot CH_3$, $CH_3 \cdot CH_2 \cdot \underset{\wedge}{C}H$, $CH_3 \cdot \overset{II}{C} \cdot CH_3$, or $CH_3 \cdot CH_2 \cdot \overset{II}{C}H$.

A further insight into the structure of the unsaturated compounds is derived from other considerations. Propylene is obtained by the elimination of HI from *n*-propyl iodide, $CH_3 \cdot CH_2 \cdot CH_2I$. The same compound is produced by the removal of HI from *iso*-

propyl iodide, $CH_3\cdot CHI\cdot CH_3$. Hence, it follows that propylene cannot have either the formula $\underset{|}{CH_2}\cdot CH_2\cdot\underset{|}{CH_2}$ or  , and therefore the remaining possibilities are $CH_3\cdot\underset{|}{CH}\cdot\underset{|}{CH_2}$, $CH_3\cdot\overset{\text{III}}{C}H\cdot\overset{\text{III}}{C}H_2$, and $CH_3\cdot CH{:}CH_2$.

*iso*Butylene, C_4H_8, is similarly formed by the elimination of HI from both iso*butyl iodide*, $(CH_3)_2C\boxed{H}\boxed{CH_2}\boxed{I}$, and *tertiary butyl iodide*, $(CH_3)_2C\boxed{I}\cdot\boxed{CH_2}\boxed{H}$. Thus, *iso*butylene can only have one of the formulæ $(CH_3)_2\underset{|}{C}\cdot\underset{|}{C}H_2$, $(CH_3)_2\overset{\text{III}}{C}\cdot\overset{\text{III}}{C}H_2$, and $(CH_3)_2C{:}CH_2$. Both these examples indicate that *the removal of hydrogen halide from an alkyl halide necessitates the elimination of a halogen atom and a hydrogen atom respectively in union with two carbon atoms directly linked together.*

Other examples serve as further illustrations of this principle. If HI be removed from a pentyl iodide, $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}CH\cdot CH_2I$, the resulting *amylene*, C_5H_{10}, should, in accordance with the principle, have the constitution $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}\underset{|}{C}\cdot\underset{|}{C}H_2$. That it actually has is proved by the fact that the addition-product obtained by the action of hydriodic acid on this amylene is not the original pentyl iodide, but one with the formula $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}CI\cdot CH_3$, as is established by replacement of I by OH, and comparison of the tertiary alcohol thus obtained with that of the same formula prepared by the synthetic method described in **111**.

The constitution of another pentyl iodide, $(CH_3)_2CH\cdot CH_2\cdot CH_2I$, which yields C_5H_{10} on elimination of HI, may be similarly established. With hydriodic acid this amylene yields another pentyl iodide, $(CH_3)_2CH\cdot CHI\cdot CH_3$: the constitution of this compound is proved by its conversion into an alcohol which yields a ketone on oxidation, and is therefore a secondary alcohol.

Butlerow has proved that the removal of hydrogen halide is impossible when the halogen atom and hydrogen atom are not united with carbon atoms in juxtaposition to one another. He converted *iso*butylene, $(CH_3)_2C{:}CH_2$, by addition of two bromine atoms into $(CH_3)_2CBr\cdot CH_2Br$. Elimination of HBr from this dibromide produced $(CH_3)_2C\cdot CHBr$, the constitution of which is inferred from its oxidation to acetone:

$$(CH_3)_2C|{:}CHBr \rightarrow (CH_3)_2CO.$$

It was not possible again to eliminate HBr from the compound $(CH_3)_2C{:}CHBr$, *monobromobutylene*, there being no hydrogen attached to the carbon atom in direct union with the CHBr-group.

128. From the foregoing considerations it is evident that only three possible constitutional formulæ remain for the unsaturated hydrocarbons.

1. Two free bonds on two carbon atoms directly linked to one another: $R\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot R'$.

2. Tervalent carbon atoms in direct union: $R\cdot\overset{III}{C}H\cdot\overset{III}{C}H\cdot R'$.

3. A double bond between two carbon atoms: $R\cdot CH{:}CH\cdot R'$.

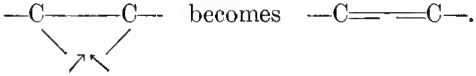
For several reasons the preference is given to the formula with the double bond. First, it would be remarkable if only carbon atoms in juxtaposition to one another could have free bonds, or be tervalent. Second, experience has shown that unsaturated compounds containing an uneven number of free bonds or tervalent carbon atoms do not exist. Next to the saturated hydrocarbons C_nH_{2n+2}, come in order of the number of hydrogen atoms, C_nH_{2n}, C_nH_{2n-2}, etc. Hydrocarbons, C_nH_{2n+1}, C_nH_{2n-1}, etc., with one or three free bonds, or tervalent carbon atoms, are unknown, all attempts to isolate methyl CH_3, ethyl C_2H_5, etc., having failed. The facts afford no support for the assumption of either free bonds or of tervalent carbon atoms. On the other hand, in forming a double linking hydrogen halide must be eliminated from adjoining carbon atoms in direct union, thus excluding the possibility of the formation of such compounds as C_nH_{2n+1}. Only the existence of the double bond, therefore, explains the observed facts.

The non-existence of free bonds in the unsaturated hydrocarbons has led by analogy to the conclusion that they are also absent from other compounds containing atoms doubly linked, trebly linked, etc., such as nitrogen in the nitriles, oxygen in the ketones, and so on.

129. The assumption of the existence of multiple bonds presents at first sight, however, certain difficulties when the power of forming addition-products possessed by all such compounds is considered. As has been stated several times, carbon bonds are only severed with difficulty (**40**), but the double carbon bond is very readily converted into a single one by formation of an addition-product. It is still more remarkable that when a substance containing a double carbon bond is oxidized, the chain is always severed at the double bond. A satisfactory explanation is afforded by the fact that when substances containing a double carbon bond are oxidized, it is often possible to prove that there is no direct rupture of the carbon chain at the double bond, but that an addition-product is first formed by the taking up of two OH-groups:

Such derivatives can often be isolated. Since oxidation always takes place at a point where it has already begun (**49**), it follows that further oxidation of such a compound must result in a severance of the carbon chain at the position previously occupied by the double bond. The breaking of the unsaturated chain by oxidation therefore depends on the formation of an intermediate addition-product, and it is only necessary to find an explanation for the ease with which the addition is effected, an object best attained by a consideration of the nature of the bonds between the atoms. An affinity or bond may be looked upon as an attraction exercised by one atom upon another. Should an atom possess more than one affinity, it is assumed that the attraction is exercised in more than one direction, and is concentrated at certain points of its surface, somewhat after the manner in which the attraction exercised by a magnet is concentrated at its two poles. Any other assumption, such as that the attracting force is equally distributed over the whole surface of an atom, would make it difficult to understand how each element could have a determinate valency. If the carbon atom is quadrivalent, there must be on its surface four such points or "poles," situated at the angles of a regular tetrahedron (**52**). When there is a single bond between two such poles on different carbon atoms, their mutual attraction causes the atoms to approach one another as closely as possible.

Von Baeyer has suggested that these poles on the surface of carbon atoms are movable. Such a movement results, however, in a certain "strain," and this tends to make the poles revert to their original position. Thus, on conversion of a single bond between two carbon atoms into a double bond, the directions of the affinities of each carbon atom must undergo an appreciable alteration:



The resulting strain is therefore a cause of the readiness with which double bonds can be severed. Von Baeyer's *strain theory* affords an explanation of other important phenomena also.

Evidently the double bond must not be regarded as a mere duplication of the single bond, as the expression "double bond" would indicate.

II. POLYMETHYLENE COMPOUNDS, C_nH_{2n}.

130. Isomeric with the olefines is a series of compounds, C_nH_{2n}, chiefly distinguished from the former by the absence of, or at least a diminution in, the power of forming addition-products. Most of these compounds are very stable: thus pentamethylene, C_5H_{10}, closely resembles *n*-pentane, C_5H_{12}. The methods for the formation of these compounds make it evident that there is a ring or closed carbon chain in the molecule (**282–286**).

III. HYDROCARBONS, C_nH_{2n-2}.

131. Two structures are possible for these compounds, which contain four hydrogen atoms less than the corresponding paraffins. Hydrocarbons with two double bonds have the general formula C_nH_{2n-2}; for example,

$$CH_2{:}CH{\cdot}CH{:}CH_2.$$

Vinylethylene

Further, substances with a *triple bond* have the same general formula; for example,

$$\underset{\text{Allylene}}{CH_3 \cdot C \equiv CH.}$$

The triple linking here is assumed for reasons similar to those applicable to the double bond in the olefines (**128**).

A. HYDROCARBONS WITH TRIPLE BONDS.

Nomenclature.

132. The first member, C_2H_2, is called *acetylene:* the second, C_3H_4, *allylene:* the higher members are regarded as substituted acetylenes; thus C_4H_6 is called *ethylacetylene;* C_6H_{10}, *butylacetylene;* and so on.

Methods of Formation.

1. By the dry distillation of complex compounds such as coal; hence the occurrence of acetylene in coal-gas.

2. By the withdrawal of two molecules of hydrogen halide from compounds of the formula $C_nH_{2n}X_2$, where X represents a halogen atom, these compounds having been previously formed by the addition of halogen to alkylenes:

$$\underset{\text{Ethylene bromide}}{CH_2Br—CH_2Br} - 2HBr = \underset{\text{Acetylene}}{CH \equiv CH.}$$

The elimination of hydrogen halide is effected by heating with alcoholic potash.

A general method for the preparation of unsaturated compounds is furnished by this method of adding on halogen, followed by the removal of hydrogen halide. Thus from C_nH_{2n+2}, $C_nH_{2n+1}X$ is obtained by the action of chlorine or bromine. Heating with alcoholic potash converts this into C_nH_{2n}, from which $C_nH_{2n}Br_2$ is got by the action of bromine, and is converted into C_nH_{2n-2} by abstraction of 2HBr. This compound can again form an addition-product with bromine, and so on.

3. By the elimination of 2HX from compounds of the formula $C_nH_{2n}X_2$, previously formed by the action of phosphorus pentahalide upon aldehydes or ketones:

$$\underset{\text{Ethylidene chloride}}{CH_3\cdot CHCl_2} - 2HCl = \underset{\text{Acetylene}}{CH{\equiv}CH}.$$

$$\underset{\text{Chloroacetone}}{CH_3\cdot CCl_2\cdot CH_3} - 2HCl = \underset{\text{Allylene}}{CH_3\cdot C{\equiv}CH}.$$

It might be anticipated that the removal of hydrogen halide would take place as indicated in the second method, with the production of two double bonds:

$$CH_3\cdot CCl_2\cdot CH_3 - 2HCl = CH_2{=}C{=}CH_2,$$

or

$$CH_3\cdot CHBr\cdot CHBr\cdot CH_3 - 2HBr = CH_2{=}CH\cdot CH{=}CH_2.$$

This is not found to be the case. The formula of the resulting product can be determined, for example, by a study of its bromine addition-products, and also from the reactions characteristic of compounds containing the group $\equiv CH$, described in the next paragraph.

Some of the hydrocarbons prepared by the foregoing methods exhibit a characteristic behaviour towards an ammoniacal solution of cuprous chloride or of a silver salt, which affords a ready means of recognizing them. By replacement of hydrogen, they yield metallic derivatives, insoluble in the ammoniacal solution or in water, which separate out as a voluminous precipitate. These compounds are explosive, the copper yellow or red, and the silver white. Acetylene, and of its higher homologues, those derived from the dihalogen compounds of the aldehydes, yield these metallic compounds. The method of formation of these homologues shows that they contain the group $\equiv CH$:

$$C_nH_{2n+1}\cdot CH_2\cdot CHO \rightarrow C_nH_{2n+1}\cdot CH_2\cdot CHCl_2 \rightarrow C_nH_{2n+1}\cdot C{\equiv}CH.$$

From this it may be concluded that *the presence of the group* $\equiv CH$ *is essential to the yielding of metallic derivatives:* it is the hydrogen of this group which is replaced by metals. In support of this view is the fact that only the dichloro-derivatives of the methylketones (110) can be transformed into hydrocarbons yielding metallic compounds:

$$C_nH_{2n+1}\cdot CO\cdot CH_3 \rightarrow C_nH_{2n+1}\cdot CCl_2\cdot CH_3 \rightarrow \underset{\text{Yields metallic derivatives}}{C_nH_{2n+1}\cdot C{\equiv}CH};$$

$$C_2H_5\cdot CO\cdot C_2H_5 \rightarrow C_2H_5\cdot CCl_2\cdot CH_2\cdot CH_3 \rightarrow \underset{\text{Does not yield metallic derivatives}}{C_2H_5\cdot C{\equiv}C\cdot CH_3}.$$

The isomeric hydrocarbons containing two double bonds (134) are also incapable of forming metallic compounds.

The hydrocarbons are readily liberated from their metallic derivatives by the action of dilute hydrochloric acid. This affords a means of isolating from mixtures the members of the series C_nH_{2n-2} which yield such derivatives, and of obtaining them in the pure state.

The hydrocarbons of this series can add on four halogen atoms or two molecules of a hydrogen halide. In presence of mercury salts they can take up water, forming aldehydes or ketones:

$$CH{\equiv}CH + H_2O = CH_3{\cdot}CHO.$$

$$CH_3{\cdot}C{\equiv}CH + H_2O = CH_3{\cdot}CO{\cdot}CH_3.$$

Mercury compounds are first formed by addition: thus, when allylene, C_3H_4, is passed into a solution of mercuric chloride, there is first formed a precipitate of the composition $3HgCl_2{\cdot}3HgO{\cdot}2C_3H_4$, which is converted into acetone by the action of hydrochloric acid.

The hydrocarbons of the acetylene series also yield condensation-products. The condensation sometimes takes place between three molecules: thus, acetylene, C_2H_2, condenses to benzene, C_6H_6; dimethylacetylene, C_4H_6, to hexamethylbenzene, $C_{12}H_{18}$; etc. This transformation is effected by the action of heat on acetylene, and of sulphuric acid on its homologues.

A remarkable reaction, resulting in a change in the position of the triple bond, takes place when the hydrocarbons of the series C_nH_{2n-2} containing the group $\equiv CH$ are heated to a high temperature in a sealed tube with alcoholic potash:

$$\underset{\text{Propylacetylene}}{C_2H_5{\cdot}CH_2{\cdot}C{\equiv}CH} \text{ is converted into } \underset{\text{Methylethylacetylene}}{C_2H_5{\cdot}C{\equiv}C{\cdot}CH_3}.$$

It is probable that addition at one part of the molecule is followed by the elimination of atoms from another part. The displacement of the triple linking in the instance cited is proved by the fact that although propylacetylene yields metallic derivatives, the substance obtained by heating it with alcoholic potash does not, but is converted by oxidation into propionic acid and acetic acid. This determines the position of the triple bond, since, for reasons similar to those applicable to the double bond (129), the carbon chain is broken by oxidation at the point occupied by the multiple bond. The substance obtained must therefore have the formula given above, and be methylethylacetylene.

Acetylene, C_2H_2.

133. Acetylene is a colourless gas of disagreeable odour, is somewhat soluble in water, and condenses at 18° and 83 atmospheres to a liquid boiling at −82·4°. It can be synthesized from its elements by the aid of an electric-arc discharge between carbon poles in an atmosphere of hydrogen, but the maximum yield of acetylene at 2500° is only 3·7 per cent. At the same temperature, about 1·2 per cent. of methane and a trace of ethane are simultaneously formed. The presence of acetylene can be detected by means of an ammoniacal solution of cuprous chloride, which yields a red precipitate of copper acetylene even from traces of acetylene mixed with other gases. Acetylene is also obtained as a product of the incomplete combustion of many organic substances. It is prepared on the large scale by the action of water on calcium carbide, or calcium acetylene, CaC_2:

$$CaC_2+2H_2O = Ca(OH)_2+C_2H_2.$$

The reaction is somewhat violent, and is attended with the evolution of a considerable quantity of heat. Calcium carbide is prepared by heating carbon with quicklime, CaO, in an electric furnace. Under the influence of the high temperature, the calcium liberated by the action of the carbon on the quicklime enters into combination with the excess of carbon, forming calcium carbide: when pure, it is white, but has usually a dark reddish-brown colour, due to the presence of small quantities of iron.

Acetylene can be prepared at a comparatively moderate cost by this method, and is sometimes employed as a substitute for coal-gas, since a stream of the hydrocarbon passed through a fine opening burns with an intensely luminous flame. Hitherto, partly owing to the cost of production but more to the nature of acetylene itself, its use has been attended by difficulties. It forms explosive copper acetylene with the copper of the gas-fittings: a mixture with air explodes with extreme violence, and is much more dangerous than a mixture of ordinary coal-gas and air. This is due to the fact that much heat is taken up in the formation of acetylene:

it is strongly endothermic ("Inorganic Chemistry," 97). Moreover, the limits of explosion are much wider than for any other gas, an explosive mixture being formed with air by the admixture of 3–82 per cent. of acetylene, while for coal-gas the limits are only 5–28 per cent. The velocity of propagation of combustion is also much greater for acetylene, and this augments considerably the force of the explosion.

Acetylene prepared from calcium carbide sometimes contains small quantities of sulphuretted hydrogen and phosphoretted hydrogen, to which it owes its disagreeable odour. It can be freed from the former by a solution of caustic alkali, and from the latter by a solution of mercuric chloride in hydrochloric acid. The removal of phosphoretted hydrogen is of special importance, since its presence may lead to the spontaneous ignition of the gas.

B. HYDROCARBONS WITH TWO DOUBLE BONDS.

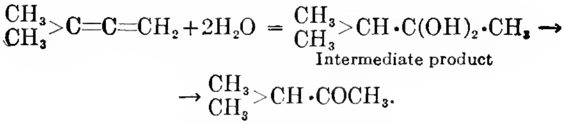
134. A hydrocarbon of this series of theoretical importance is *isoprene*, C_5H_8. It is obtained by the dry distillation of caoutchouc, and is a liquid boiling at 37°. By the union of two or more molecules, it passes into terpenes, $C_{10}H_{16}$, $C_{15}H_{24}$, etc. It is converted by concentrated hydrochloric acid into a substance strongly resembling caoutchouc, perhaps identical with it. Isoprene is proved to have the constitution ${CH_2 \atop CH_3}\!\geqslant C\cdot CH{=}CH_2$ by the addition of 2HBr, which yields a dibromide, ${CH_3 \atop CH_3}\!>CBr{-}CH_2{-}CH_2Br$, identical with that obtained from dimethylallene, ${CH_3 \atop CH_3}\!>C{=}C{=}CH_2$.

Dimethylallene is thus obtained. Two carbinol-derivatives, dimethylethylcarbinol, ${CH_3 \atop CH_3}\!>C(OH)\cdot CH_2\cdot CH_3$, and methyl*iso*propylcarbinol, ${CH_3 \atop CH_3}\!>CH\cdot CHOH\cdot CH_3$, are prepared by the method described in 111, and converted into the corresponding iodides. On elimination of HI, each iodide yields trimethylethylene, ${CH_3 \atop CH_3}\!>C{=}CH\cdot CH_3$, its formation from both iodides admitting of no other position for the double bond. Trimethylethylene takes up 2Br, forming ${CH_3 \atop CH_3}\!>CBr\cdot CHBr\cdot CH_3$. On treatment of this substance with alcoholic potash, two molecules of hydrobromic acid, 2HBr, are eliminated, with the formation of dimethylallene, ${CH_3 \atop CH_3}\!>C{=}C{=}CH_2$.

This mode of formation does not wholly preclude another arrangement of the double bonds, but other evidence proves that dimethylallene has the structural formula indicated.

1. On oxidation it yields acetone, proving the presence of the group $(CH_3)_2C=$.

2. Treatment with sulphuric acid of 50 per cent. strength converts it into methyl*iso*propylketone:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=C=CH_2+2H_2O = \underset{\text{Intermediate product}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot C(OH)_2\cdot CH_3} \rightarrow$$

$$\rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COCH_3.$$

Compounds like this intermediate product are referred to in 155.

When forming an addition-product with two univalent atoms, organic compounds containing the group $C=C-C=C$, called by THIELE a "Conjugated system," often behave peculiarly, the addition taking place at C-atoms 1 and 4, with formation of a double bond between C-atoms 2 and 3:

$$CH_2=CH\cdot CH=CH_2+Br_2 = CH_2Br\cdot CH=CH\cdot CH_2Br.$$

SUBSTITUTION-PRODUCTS OF THE UNSATURATED HYDROCARBONS.

I. UNSATURATED HALOGEN COMPOUNDS.

135. Since the saturated hydrocarbons do not themselves possess any salient characteristics, the properties of their compounds depend upon the nature of the substituents. Hitherto, only compounds with properties due to the presence in the molecule of a single group, such as hydroxyl, carboxyl, a multiple carbon bond, etc., have been described. Substances containing more than one characteristic group in the molecule must now be considered.

When these groups are present simultaneously in the same molecule, they exercise a modifying influence upon one another. The extent of this influence varies considerably, as is evident from a consideration of the different classes of *unsaturated halogen compounds*.

Halogen derivatives of the type $C_nH_{2n-1}X$ are obtained by the addition of halogen to the hydrocarbons C_nH_{2n}, and subsequent elimination of one molecule of hydrogen halide:

$$CH_2{=}CH_2 + Br_2 = CH_2Br{-}CH_2Br.$$

$$\underset{\text{Ethylene bromide}}{CH_2Br{-}CH_2Br} - HBr = \underset{\text{Vinyl bromide}}{CH_2{=}CHBr}.$$

They are also formed by removal of one molecule of hydrogen halide from compounds containing two halogen atoms in union with the same carbon atom:

$$\underset{\text{Propylidene chloride}}{CH_3{\cdot}CH_2{\cdot}CHCl_2} - HCl = \underset{\alpha\text{-Chloropropylene}}{CH_3{\cdot}CH{=}CHCl}.$$

$$\underset{\text{Chloroacetone}}{CH_3{\cdot}CCl_2{\cdot}CH_3} - HCl = \underset{\beta\text{-Chloropropylene}}{CH_3{\cdot}CCl{=}CH_2}.$$

The methods employed in the preparation of these compounds indicate that their halogen atom is in union with a carbon atom having a double bond. Their properties differ widely from those of compounds like the alkyl halides, with the halogen atom attached to a singly-linked carbon atom; and this rule is general for such compounds. The halogen atom of the alkyl halides is especially able to take part in double decompositions: it is replaceable by hydroxyl, an alkoxyl-group, an acid-residue, the amino-group, and so on.

This aptitude for double decomposition is almost lacking in compounds with halogen in union with a doubly-linked carbon atom. Alkalis do not convert them into alcohols, nor alkoxides into ethers: but invariably, when they do react, hydrogen halide is eliminated, with formation of hydrocarbons of the series C_nH_{2n-2}.

An isomeride of *α-chloropropylene* and *β-chloropropylene*, which have been referred to above, is called *allyl chloride*. Its halogen atom takes part in double decompositions as readily as the halogen atom of an alkyl chloride. Allyl chloride is obtained by the action of phosphorus pentachloride upon allyl alcohol, prepared by a method described in 158. This alcohol yields *n*-propyl alcohol by addition of hydrogen, and its hydroxyl-group must therefore be at the end of the carbon chain. Hence, the halogen atom in allyl chloride must also be at the end of the chain, since it takes the place of the hydroxyl-group. Given the constitutions of α-propylene chloride and β-propylene chloride, which are deduced from those of propionaldehyde and acetone, the allyl halides can only have the constitutional formula

$$CH_2{=}CH \cdot CH_2X.$$

The halogen atom is attached to a singly-linked carbon atom, and retains its normal character despite the presence of a double bond in the molecule.

The influence exerted upon the character of a halogen atom by its position in the molecule of an unsaturated compound affords a means of determining whether it is attached to a singly-linked or doubly-linked carbon atom, the indication being its possession or lack of the power to take part in double decompositions.

The following are examples of individual members of the series. *Vinyl chloride* $CH_2{:}CHCl$ is a gas, *vinyl bromide* $CH_2{:}CHBr$ a liquid of ethereal odour. Both these compounds polymerize readily.

Allyl chloride, allyl bromide, and *allyl iodide,* boil respectively at 46°, 70°, and 103°. They are often employed in syntheses to introduce an unsaturated group into a compound. They have a characteristic odour resembling that of mustard.

The *propargyl compounds,* $CH{\equiv}C{\cdot}CH_2X$, are a type of the series $C_nH_{2n-3}X$. Their constitution is inferred from the facts that they yield metallic derivatives, indicating the presence of the group $\equiv CH$, and that their halogen atoms are capable of taking part in double decompositions, proving their union with a singly-linked carbon atom. They are obtained from propargyl alcohol (**138**) by the action of phosphorus pentahalides, and are liquids of pungent odour.

Bromoacetylidene, $CHBr{:}C$, which is assumed by NEF to contain a bivalent carbon atom, can be obtained from acetylene bromide, $CHBr{:}CHBr$, by treatment with alcoholic potash. It is a gas, boils at −2°, and takes fire spontaneously in the air. Its solution in alcohol is phosphorescent, owing to slow oxidation, and the gas itself has an odour very similar to that of phosphorus.

II. UNSATURATED ALCOHOLS.

136. The hydroxyl-group of the *unsaturated alcohols* may be attached to a singly-linked or to a doubly-linked carbon atom:

$$\underset{\text{Allyl alcohol}}{CH_2{:}CH{\cdot}CH_2OH}, \qquad \underset{\text{Vinyl alcohol}}{CH_2{:}CH{\cdot}OH}.$$

Few compounds of the type of *vinyl alcohol* are known. It is found that reactions which might be expected to yield them generally result in the formation of their isomerides. Thus, when water is abstracted from glycol, $CH_2OH{\cdot}CH_2OH$, there results, not vinyl alcohol, $CH_2{=}CHOH$, but an isomeride, acetaldehyde, $CH_3{-}C{<}^{H}_{O}$.

When β-bromopropylene, $CH_3{\cdot}CBr{:}CH_2$, is heated with water, there is formed not β-hydroxypropylene, $CH_3{\cdot}C(OH){:}CH_2$, but the isomeric acetone, $CH_3{\cdot}CO{\cdot}CH_3$. The rule is that when a grouping of the atoms in the form $-CH{:}C(OH)-$ would be expected, a transformation into $-CH_2{\cdot}CO-$ usually occurs. Although most substances containing hydroxyl attached to a doubly-linked carbon atom are unstable, they have a tendency to become transformed into isomerides. Compounds do exist, however, in which the group —CH:C(OH)— is stable (254–256).

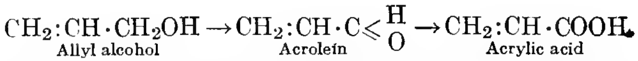
The following compounds either contain hydroxyl in union with a doubly-linked carbon atom, or are related to substances of that type.

Vinyl alcohol, $CH_2{:}CHOH$, so called because it contains the *vinyl*-group, $CH_2{:}CH$—, is probably present in ordinary ethyl ether owing to partial oxidation. When such ether is agitated with an alkaline solution of a mercury salt, a precipitate of the composition $Hg_3Cl_2O_2C_2H_3$ is formed, and on treatment with hydrogen halide yields vinyl-compounds.

A vinyl-derivative of great physiological importance, called *neurine*, is formed in the putrefactive decay of flesh, and in other fermentation-processes. Its constitution is $(CH_3)_3N{<}\begin{matrix}CH{:}CH_2\\OH\end{matrix}$, as is indicated by synthesis. When trimethylamine reacts with ethylene bromide, a substituted ammonium bromide of the formula $(CH_3)_3N{<}\begin{matrix}CH_2{\cdot}CH_2Br\\Br\end{matrix}$ is obtained. HBr is eliminated from the group $—CH_2{\cdot}CH_2Br$ by the action of moist silver oxide, the bromine atom attached to nitrogen being simultaneously replaced by hydroxyl. A substance of the constitution indicated is thus obtained, and is in all respects similar to neurine.

Allyl Alcohol, $CH_2{:}CH{\cdot}CH_2OH$.

137. Many unsaturated alcohols containing hydroxyl attached to a singly-linked carbon atom are known. The most important is *allyl alcohol*, the preparation of which is described in 158. Its constitution is inferred from that of the chlorine derivative formed by the action of phosphorus pentachloride (135); as well as from that of the products obtained by oxidation, by which allyl alcohol is converted first into an aldehyde, *acroleïn*, and then into *acrylic acid:*



$$\underset{\text{Allyl alcohol}}{CH_2{:}CH{\cdot}CH_2OH} \rightarrow \underset{\text{Acroleïn}}{CH_2{:}CH{\cdot}C{<}\begin{matrix}H\\O\end{matrix}} \rightarrow \underset{\text{Acrylic acid}}{CH_2{:}CH{\cdot}COOH.}$$

Allyl alcohol must therefore contain the group $—CH_2OH$, characteristic of primary alcohols.

Allyl alcohol is a liquid of irritating odour, solidifying at −50°, and boiling at 96·5°, and is miscible with water in all proportions. Its specific gravity at 0° is 0·872. It forms addition-products with the halogens and with hydrogen, with the latter yielding *n*-propyl alcohol.

Many other compounds containing the allyl-group, $CH_2:CH\cdot CH_2—$, are known, among them *allyl sulphide* $(CH_2:CH\cdot CH_2)_2S$, the principal constituent of oil of garlic. It is synthetically obtained by the action of potassium sulphide, K_2S, on allyl iodide.

It is apparent that the influence of the double bond in the unsaturated halogen compounds and alcohols is very pronounced when it is situated in the immediate neighbourhood of halogen or hydroxyl, but that otherwise its influence is much less marked. *When two groups are situated in immediate proximity to one another in the same molecule, each group exercises a strong influence upon the properties of the other.*

Propargyl Alcohol, $CH\equiv C\cdot CH_2OH$.

138. *Propargyl alcohol* contains a triple bond, and is prepared from tribromohydrin, $CH_2Br\cdot CHBr\cdot CH_2Br$ (153). Caustic potash converts this substance into $CH_2:CBr\cdot CH_2Br$, which on treatment with potassium acetate and saponification yields $CH_2:CBr\cdot CH_2OH$, since only the terminal Br-atom is capable of taking part in a double decomposition (135). When this alcohol is again brought into contact with caustic potash, HBr is eliminated, with formation of propargyl alcohol, the constitution of which is indicated by this method of formation and also by its properties. The presence of the group $\equiv CH$ is indicated by the formation of metallic derivatives: on oxidation it yields *propiolic acid*, $CH\equiv C\cdot COOH$, with the same number of carbon atoms, proving that it is a primary alcohol.

Propargyl alcohol is a liquid of agreeable odour, soluble in water, and boiling at 114°–115°: its specific gravity at 21° is 0·963. Its metallic derivatives are explosive.

MONOBASIC UNSATURATED ACIDS.

I. ACIDS OF THE OLEÏC SERIES, $C_nH_{2n-2}O_2$.

139. The acids of the *oleïc series* can be obtained from the saturated acids $C_nH_{2n}O_2$ by the methods generally applicable to the conversion of saturated into unsaturated compounds.

1. Substitution of one hydrogen atom in the alkyl-group of a saturated acid by a halogen atom, and subsequent elimination of hydrogen halide by heating with alcoholic potash.

2. Removal of the elements of water from the monohydroxy-acids:

$$\underset{\beta\text{-Hydroxybutyric acid}}{CH_3\cdot CHOH\cdot CH_2\cdot COOH} - H_2O = \underset{\text{Crotonic acid}}{CH_3\cdot CH:CH\cdot COOH}.$$

The acids of this series can also be prepared from unsaturated compounds by

3. Oxidation of the unsaturated alcohols and aldehydes.

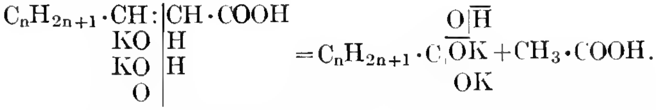
4. The action of potassium cyanide on unsaturated halogen compounds, such as allyl iodide, and hydrolysis of the resulting nitrile.

Nomenclature.

140. Most of the acids of the oleïc series are named after the substances from which they were first obtained, but a few of the middle members have names indicating the number of carbon atoms in the molecule. The first member, $CH_2:CH\cdot COOH$, is called *acrylic acid:* others are *crotonic acid,* $C_4H_6O_2$; *angelic acid and tiglic acid,* $C_5H_8O_2$; *undecylenic acid,* $C_{11}H_{20}O_2$; *oleïc acid,* $C_{18}H_{34}O_2$; *erucic acid,* $C_{22}H_{42}O_2$; etc.

Properties.

141. In common with all compounds containing a double bond, the acids of this series possess the power of forming addition-products. They are "stronger" acids than the corresponding fatty acids containing the same number of carbon atoms in the molecule: thus, the value of the constant 10^4K (**93**) for propionic acid, $C_3H_6O_2$, is 0·134; for acrylic acid, $C_3H_4O_2$, 0·56; for butyric acid, $C_4H_8O_2$, 0·149; for crotonic acid, $C_4H_6O_2$, 0·204; etc. The double bond renders the acids of the oleïc series much more susceptible to oxidation than those of the fatty series (**129**). The former are converted by energetic oxidizers into two saturated acids, but when the reaction is made less energetic by using a dilute solution of potassium permanganate, a dihydroxy-acid containing the group —CHOH·CHOH— is formed as an intermediate product, and on further oxidation the chain is severed at the bond between these two carbon atoms (**129**). This behaviour affords a means of determining the position of the double bond in the molecule. A breaking down of the molecule with formation of saturated fatty acids also results on fusion of an unsaturated acid with caustic potash in presence of air:



$$\begin{array}{r|l} C_nH_{2n+1}\cdot CH: & CH\cdot COOH \\ KO & H \\ KO & H \\ O & \end{array} = C_nH_{2n+1}\cdot C\begin{array}{l} O|\overline{H} \\ \overline{OK} \\ OK \end{array} + CH_3\cdot COOH.$$

Formerly the reaction was employed to determine the position of the double bond, on the assumption that the division of the molecule was effected at the point where this bond was situated in the first instance. It is now known that under the influence of fused caustic potash, or even by boiling with a solution of caustic soda, the position of the double bond is displaced nearer that of the carboxyl-group. Fusion with caustic potash cannot, therefore, be employed as a means of determining the position of double bonds.

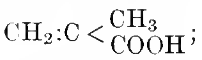
Acrylic Acid, $CH_2:CH\cdot COOH$.

142. *Acrylic acid* is obtained by the elimination of HI from β-iodopropionic acid, $CH_2I\cdot CH_2\cdot COOH$. It is a liquid of pungent odour, boiling at 140°, and is reduced by nascent hydrogen to pro-

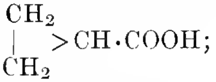
Acids of the formula $C_4H_6O_2$.

143. The theoretically possible acids of the formula $C_4H_6O_2$ are

1. $CH_2{:}CH\cdot CH_2\cdot COOH$; 2. $CH_3\cdot CH{:}CH\cdot COOH$;

3. 

$CH_2{:}C{<}\begin{matrix}CH_3\\COOH\end{matrix}$;

4. 

$\begin{matrix}CH_2\\|\\CH_2\end{matrix}{>}CH\cdot COOH$;

but five acids of the formula $C_4H_6O_2$ are known.

An acid of the constitution indicated in formula 1, *vinylacetic acid,* can be obtained by the action of carbon dioxide on allyl magnesium bromide, and decomposition of the primary product by acidulated water:

$$CH_2{:}CH\cdot CH_2MgBr+CO_2=CH_2{:}CH\cdot CH_2\cdot CO_2MgBr;$$

$$CH_2{:}CH\cdot CH_2\cdot CO_2MgBr+H_2O=$$
$$=CH_2{:}CH\cdot CH_2\cdot COOH+MgBr\cdot OH.$$

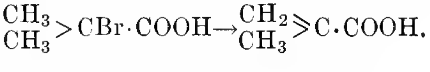
Its formation by the action of potassium cyanide on allyl iodide, and hydrolysis of the nitrile thus formed, might be expected:

$$\underset{\text{Allyl iodide}}{CH_2{:}CH\cdot CH_2I}\rightarrow CH_2{:}CH\cdot CH_2CN\rightarrow CH_2{:}CH\cdot CH_2\cdot COOH.$$

Actually, however, an acid of formula 2 is obtained, *solid crotonic acid,* which melts at 71° and boils at 180°: careful oxidation with permanganate converts it into oxalic acid, HOOC—COOH, a proof of its constitution. It follows that during the reaction the position of the double bond must have changed.

iso*Crotonic acid*, melting at 15·5° and boiling at 172°, has also constitution 2, because, on the one hand, like solid crotonic acid it can be reduced to *n*-butyric acid, proving that it too contains a normal carbon chain; on the other, it is converted by careful oxidation into oxalic acid. Ordinary constitutional formulæ are incapable, therefore, of accounting for the isomerism of these acids; which is explained in **170.**

An acid with formula 3 is obtained by the elimination of HBr from bromo*iso*butyric acid; it is called *methacrylic acid:*



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CBr\cdot COOH\rightarrow\begin{matrix}CH_2\\CH_3\end{matrix}{\geqslant}C\cdot COOH.$$

The acid of formula 4 is described in **282.**

Oleïc Acid, $C_{18}H_{34}O_2$.

144. *Oleïc acid* is obtained by the saponification of oils and soft fats (**91**). To separate it from the saturated fatty acids, stearic and palmitic, simultaneously liberated, the lead salt is prepared. Lead oleate is soluble in ether, while lead palmitate and stearate are not. The oleïc acid is liberated from the lead oleate by treatment with acids.

At ordinary temperatures, oleïc acid is a liquid without odour and of an oily nature. It melts at 14°. It oxidizes readily in the air, and cannot be distilled at ordinary pressures without decomposition.

Oleïc acid contains a normal carbon chain, since on reduction it yields stearic acid.

> Krafft has proved the normal structure of stearic acid by converting it step by step into acids with a smaller number of carbon atoms. When submitted to dry distillation in a vacuum, barium stearate and barium acetate form a ketone, $C_{17}H_{35}\cdot CO\cdot CH_3$:
>
> $$C_{17}H_{35}\cdot\boxed{COOba^{*}+baO\cdot}OC\cdot CH_3 \rightarrow C_{17}H_{35}\cdot CO\cdot CH_3.$$
>
> Barium stearate   Barium acetate   Margarylmethylketone
>
> On oxidation, this ketone yields acetic acid and an acid of the formula $C_{17}H_{34}O_2$. This proves that the ketone contains a CH_2-group next to the carbonyl-group, and has the formula $C_{16}H_{33}\cdot CH_2\cdot CO\cdot CH_3$, for only from such a compound could oxidation produce an acid with seventeen carbon atoms. This acid, $C_{17}H_{34}O_2$ (*margaric acid*), is similarly transformed into a ketone, $C_{16}H_{33}\cdot CO\cdot CH_3$, which on oxidation yields an acid $C_{16}H_{32}O_2$. The formula of margaric acid must therefore be $C_{15}H_{31}\cdot CH_2\cdot COOH$, and that of stearic acid, $C_{15}H_{31}\cdot CH_2\cdot CH_2\cdot COOH$. The acid $C_{16}H_{32}O_2$, *palmitic acid*, is in its turn converted into a ketone, and the process continued until *capric acid*, $C_{10}H_{20}O_2$, is obtained. This acid has been proved by synthesis (**251**, 1) to contain a normal carbon chain.

The presence of a double bond in oleïc acid is indicated by its forming an addition-product with bromine, and by its power of reducing an alkaline permanganate solution (**123**). The double

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* ba = ½Ba.

bond is situated at the centre of the chain, the constitution of oleïc acid being

$$CH_3 \cdot (CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_7 \cdot COOH.$$

This constitution is inferred from the products of careful oxidation, which yields *pelargonic acid*, $C_8H_{17} \cdot COOH$, and *azelaïc acid*, $HOOC \cdot (CH_2)_7 \cdot COOH$.

Oleïc acid reacts in a remarkable manner with nitrous acid, even when brought into contact with a mere trace of this substance. The best method is to pass the red gaseous mixture of nitrogen peroxide and nitric oxide, obtained by heating arsenic trioxide with nitric acid, into oleïc acid, or to add nitric acid of specific gravity 1·25. The oleïc acid soon solidifies, having been converted into an isomeride, *elaïdic acid*. The reaction is called the "elaïdic transformation." Other acids of this series are similarly transformed: thus, *erucic acid*, $C_{22}H_{42}O_2$, is converted by a trace of nitrous acid into *brassidic acid*.

Elaïdic acid has the same structural formula as oleïc acid, the double bond occupying a similar position in the molecule of each, since each acid readily forms a bromine addition-product from which elimination of 2HBr yields *stearolic acid*, $C_{18}H_{32}O_2$:

$$\underset{\text{Oleïc and elaïdic acids}}{C_{18}H_{34}O_2} \rightarrow \underset{\text{Bromine addition-product}}{C_{18}H_{34}Br_2O_2} \rightarrow \underset{\text{Stearolic acid}}{C_{18}H_{32}O_2}.$$

Oleïc acid and elaïdic acid yield the same hydroxystearic acid by the addition of one molecule of water, a reaction effected by the action of concentrated sulphuric acid. Their isomerism is, therefore, like that of erucic acid and brassidic acid, analogous to the isomerism of the two crotonic acids (143).

II. ACIDS OF THE PROPIOLIC SERIES, $C_nH_{2n-4}O_2$.

145. The acids of the *propiolic series* have one triple bond, or two double bonds, in the molecule. The first-named are formed by the action of carbon dioxide upon the sodium compounds of the acetylene hydrocarbons:

$$CH{\equiv}CNa + CO_2 = \underset{\text{Sodium propiolate}}{CH{\equiv}C \cdot COONa}.$$

The α-carbon atom of these acids has a triple bond, and such acids are very readily decomposed into an acetylene hydrocarbon and CO_2; for example, by heating their silver salts.

A general method for the preparation of acids with triple bonds involves the addition of two bromine atoms to acids containing a double bond, and subsequent elimination of 2HBr:

$$\underset{\text{Crotonic acid}}{CH_3 \cdot CH:CH \cdot COOH} \rightarrow \underset{\text{Dibromobutyric acid}}{CH_3 \cdot CHBr \cdot CHBr \cdot COOH} \rightarrow$$

$$\rightarrow \underset{\text{Tetrolic acid}}{CH_3 \cdot C \vdots C \cdot COOH}.$$

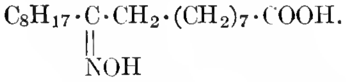
In presence of concentrated sulphuric acid, substances with a triple bond take up water with formation of ketones:

$$—C{\equiv}C— \rightarrow —CH_2 \cdot CO—.$$

In this manner stearolic acid is converted into a ketostearic acid of the formula

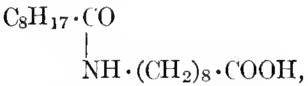
$$C_8H_{17} \cdot CO \cdot CH_2 \cdot (CH_2)_7 \cdot COOH,$$

and treatment with hydroxylamine transforms this into the corresponding oxime:



$$C_8H_{17} \cdot \underset{\displaystyle NOH}{\overset{}{C}\Vert} \cdot CH_2 \cdot (CH_2)_7 \cdot COOH.$$

Under the influence of concentrated sulphuric acid, this oxime undergoes the Beckmann transformation (112), among the products being the substituted acid amide



$$\begin{array}{l} C_8H_{17} \cdot CO \\ \qquad\quad | \\ \qquad\quad NH \cdot (CH_2)_8 \cdot COOH, \end{array}$$

which is proved to have this formula by its decomposition into pelargonic acid, $C_8H_{17} \cdot COOH$, and the 9-aminononoïc* acid, $NH_2 \cdot (CH_2)_8 \cdot COOH$, by the action of fuming hydrochloric acid. This is a confirmation of the constitution above indicated for oleïc acid and elaïdic acid, since they can be converted into stearolic acid in the manner already described.

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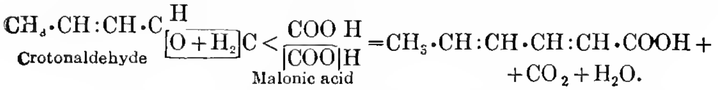
* If the carboxyl-carbon atom is denoted by 1, the amino-group is in union with the ninth carbon atom of the chain.

Acids with Two Double Bonds, $C_nH_{2n-4}O_2$.

146. Very few of these acids are known. Among them is *sorbic acid*, $C_6H_8O_2$, a crystalline substance melting at 134·5°. It is present in the unripe berries of the mountain-ash, and its constitution $CH_3\cdot CH:CH\cdot CH:CH\cdot COOH$ is proved by its synthesis, which is effected by the condensation of malonic acid with crotonaldehyde under the influence of pyridine as a condensing agent:



$$\underset{\text{Crotonaldehyde}}{CH_3\cdot CH:CH\cdot C\overset{H}{\boxed{O+H_2}}}C<\underset{\text{Malonic acid}}{\begin{matrix}COO\,H\\ \boxed{COO}H\end{matrix}}=CH_3\cdot CH:CH\cdot CH:CH\cdot COOH+ \\ +CO_2+H_2O.$$

Isomeric with stearolic acid is *linoleic acid*, $C_{18}H_{32}O_2$, obtained by the saponification of linseed-oil. When carefully oxidized with potassium permanganate it is converted into a tetrahydroxystearic acid, $C_{18}H_{32}O_2(OH)_4$, proving the presence of two double bonds in the molecule.

UNSATURATED ALDEHYDES AND KETONES.

147. The lowest unsaturated aldehyde is *acroleïn*, $CH_2{:}CH\cdot CHO$. It is obtained by removal of water from glycerol, which is best effected by heating with potassium pyrosulphate, $K_2S_2O_7$. It is a colourless liquid, boiling at 52·4°, and has an extremely powerful, penetrating odour, to which it owes its name (*acer*, sharp, and *oleum*, oil). The disagreeable, pungent smell produced when a tallow candle or an oil-lamp is extinguished is due to the formation of acroleïn. On reduction, it yields allyl alcohol, from which it is regenerated by careful oxidation. It is converted into acrylic acid by further oxidation.

It has the properties peculiar to aldehydes—the susceptibility to reduction and oxidation, resinification in presence of alkalis, and the power of forming polymerization-products. It possesses this last property in such a marked degree that it usually becomes completely converted into a polymeride in the course of a few days or even hours, probably under the catalytic influence of traces of impurities. The presence of the double bond in acroleïn modifies to some extent the aldehydic character. This is exhibited in its behaviour towards ammonia, with which it does not combine like acetaldehyde (**113**), but in accordance with the equation

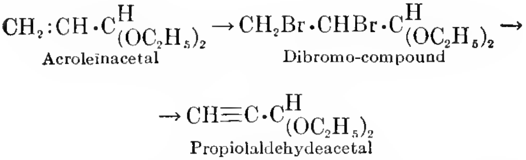
$$2C_3H_4O + NH_3 = C_6H_9ON + H_2O.$$

Acroleïn-ammonia is an amorphous, basic substance, is soluble in water, and in its appearance and behaviour towards water bears a close resemblance to glue.

Acroleïn does not unite with one molecule of an acid sulphite, but with two, yielding a compound from which the aldehyde cannot be regenerated by the action of acids, which eliminate only one molecule of the acid sulphite. This indicates that the other molecule of acid sulphite has been added at the double bond.

148. *Crotonaldehyde*, $CH_3{\cdot}CH{:}CH{\cdot}CHO$, results on elimination of water from aldol, $CH_3{\cdot}CH\boxed{OH}{\cdot}CH\boxed{H}{\cdot}C^{H}_{O}$ (115), by heating to 140°. It is a liquid boiling at 104°–105°, and is converted by oxidation with silver oxide into solid crotonic acid (143), proving that it has the constitution indicated.

Propiolaldehyde, $CH{\equiv}C{\cdot}C{<}^{H}_{O}$, can be obtained from acroleïn-acetal by the addition of two bromine atoms, and subsequent removal by means of caustic potash of 2HBr from the addition-product thus formed:



$$CH_2{:}CH{\cdot}C^{H}_{(OC_2H_5)_2} \rightarrow CH_2Br{\cdot}CHBr{\cdot}C^{H}_{(OC_2H_5)_2} \rightarrow$$

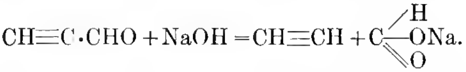
Acroleïnacetal Dibromo-compound

$$\rightarrow CH{\equiv}C{\cdot}C^{H}_{(OC_2H_5)_2}$$

Propiolaldehydeacetal

Propiolaldehydeacetal is converted by warming with dilute sulphuric acid into the corresponding aldehyde, which has the same irritating action on the mucous membrane as acroleïn.

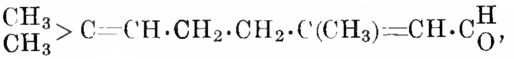
The behaviour of propiolaldehyde towards alkalis is remarkable. It decomposes into acetylene and formic acid:



$$CH{\equiv}C{\cdot}CHO + NaOH = CH{\equiv}CH + C{\lessgtr}^{H}_{O}{-}ONa.$$

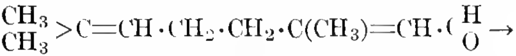
149. An important unsaturated aldehyde is *geranial* (*citral*), $C_{10}H_{16}O$, characterized by its agreeable odour. It is a constituent of various essential oils; among them oil of orange-rind, the cheap oil of lemon-grass, and oil of citron. At the ordinary temperature it is liquid, and boils at 110°–112° under a pressure of 12 mm. Its aldehydic nature is shown by its reduction to an alcohol, *geraniol*, and its oxidation to an acid with the same number of carbon atoms, *geranic acid*.

Geranial has the structural formula



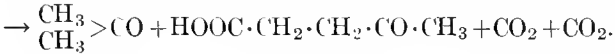
$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3){=}CH{\cdot}C^{H}_{O},$$

since on oxidation it yields acetone, lævulic acid (252), and carbon dioxide, the molecule breaking down at the double bonds:



$$\begin{matrix}CH_3\\CH_3\end{matrix}>C{=}CH\cdot CH_2\cdot CH_2\cdot C(CH_3){=}CH\cdot C\begin{matrix}H\\O\end{matrix}\rightarrow$$

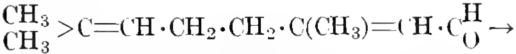
Geranial



$$\rightarrow\begin{matrix}CH_3\\CH_3\end{matrix}>CO+HOOC\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3+CO_2+CO_2.$$

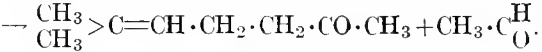
Acetone Lævulic acid Carbon dioxide

When boiled with a solution of potassium carbonate, geranial takes up one molecule of water, forming *methylheptenone* and acetaldehyde:



$$\begin{matrix}CH_3\\CH_3\end{matrix}>C{=}CH\cdot CH_2\cdot CH_2\cdot C(CH_3){=}CH\cdot C\begin{matrix}H\\O\end{matrix}\rightarrow$$

Geranial



$$\rightarrow\begin{matrix}CH_3\\CH_3\end{matrix}>C{=}CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3+CH_3\cdot C\begin{matrix}H\\O\end{matrix}.$$

Methylheptenone Acetaldehyde

On oxidation, methylheptenone also yields acetone and lævulic acid. This reaction indicates its constitution, which is further proved by synthesis.

Baryta-water converts a mixture of geranial and acetone into a condensation-product, pseudo*ionone:*

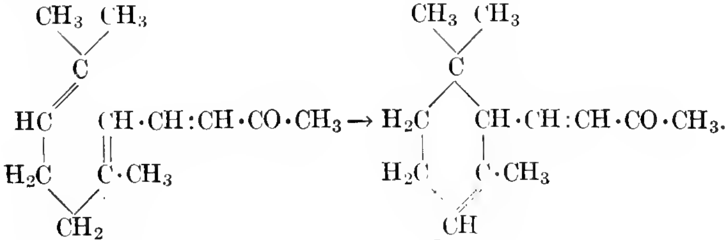
$$(CH_3)_2C{=}CH\cdot CH_2\cdot CH_2\cdot C(CH_3){=}CH\cdot CHO+H_2CH\cdot CO\cdot CH_3=$$

Geranial Acetone

$$=H_2O+(CH_3)_2C{=}CH\cdot CH_2\cdot CH_2\cdot C(CH_3){=}CH\cdot CH{=}CH\cdot CO\cdot CH_3.$$

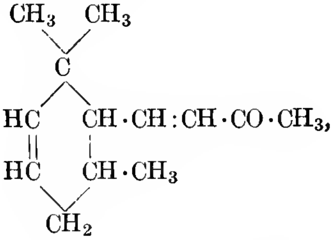
*pseudo*Ionone

When boiled with dilute sulphuric acid, *pseudo*ionone yields *ionone:*



*pseudo*Ionone Ionone

The structure of ionone is proved by its decomposition-products. It is manufactured as an artificial perfume, as it has a powerful, violet-like odour, and is closely related to *irone*, the active principle of violets. The formula of irone is



which differs from that of ionone only in the position occupied by the double bond in the carbon ring.

COMPOUNDS CONTAINING MORE THAN ONE SUBSTITUENT.

I. HALOGEN DERIVATIVES OF METHANE.

150. The halogen derivatives of the saturated hydrocarbons obtained by replacement of a single hydrogen atom by halogen are called alkyl halides, and are described in **58.** This chapter treats of the compounds formed by exchange of more than one hydrogen atom for halogen.

It is possible to replace all four hydrogen atoms in methane, in successive stages, by the direct action of chlorine or bromine in presence of sunlight. Iodine does not react with methane, or with its homologues, while the action of fluorine is very energetic, effecting complete substitution.

In practice, however, this is not the method adopted for the preparation of the compounds CH_2X_2, CHX_3, or CX_4. They are obtained from the trihalogen derivatives: these are readily prepared by another method, and on chlorination or bromination yield tetrachloromethane or tetrabromomethane; on reduction they are converted into dihalogen-substituted methanes. On account of their important therapeutic properties, the compounds CHX_3 are prepared on the large scale.

Chloroform, $CHCl_3$.

151. *Chloroform* is obtained by distilling alcohol—or on the manufacturing scale, acetone—with bleaching-powder. This reaction involves simultaneous oxidation and chlorination, and it is assumed that aldehyde is first produced by oxidation of the alcohol, and is then transformed into *trichloroaldehyde*, or *chloral*, $CCl_3 \cdot CHO$.

This substance is converted by bases, in this instance by the slaked lime present in the bleaching-powder, into chloroform and formic acid (201).

Chloroform is a liquid boiling at 61°, and solidifying at −70°. Its specific gravity at 15° is 1·498: it is very slightly soluble in water, and possesses a characteristic ethereal odour and sweet taste. Its prolonged inhalation produces unconsciousness, whence it derives its value as an anæsthetic in surgical operations.

> Its use for this purpose is not wholly unattended with danger. Notwithstanding the fund of experience resulting from the frequency of its application, it occasionally happens that the inhalation of chloroform is attended by fatal results. Ordinary ether and ethyl chloride are less dangerous, do not produce such disagreeable after-effects, and hence have latterly been preferred as anæsthetics (63).

Chloroform is a somewhat unstable substance, decomposing under the influence of light and air, and yielding chlorine, hydrochloric acid, and carbon oxychloride, $COCl_2$. This decomposition can be almost prevented by adding one per cent. of alcohol, and keeping the chloroform in bottles of non-actinic glass. The preservative action of alcohol probably depends upon its combination with the decomposition-products of the chloroform, thus preventing their exercising a catalytic, accelerating influence on the decomposition. The halogen atoms of chloroform take part in double decompositions: thus, sodium ethoxide yields the ethyl ester of orthoformic acid:

$$CH\boxed{Cl_3+3Na}\cdot OC_2H_5=CH(OC_2H_5)_3+3NaCl.$$

Formic acid can be obtained by warming chloroform with dilute alkalis, orthoformic acid being probably formed first, although it has not been isolated. When chloroform is treated with a 40 per cent. aqueous solution of caustic potash, carbon monoxide is evolved: it is assumed that chloromethylene, CCl_2, is formed as an intermediate product.

When chloroform is warmed with alcoholic ammonia and caustic potash, its three chlorine atoms are replaced by nitrogen, with production of potassium cyanide. The formation of *iso*nitriles from chloroform, alcoholic potash, and primary amines, has been already mentioned (84).

Methylene chloride, CH_2Cl_2, is obtained from chloroform by reduction with zinc and hydrochloric acid in alcoholic solution. It is a liquid, boils at 40°, and has a specific gravity of 1·337.

Tetrachloromethane, or *carbon tetrachloride*, CCl_4, produced by the action of chlorine on chloroform or carbon disulphide, is also a liquid, and boils at 76°. When heated with excess of water at 250° it yields HCl and CO_2. Its specific gravity is 1·593 at 20°: the high specific gravities of these polychloro-compounds is noteworthy. The bromine and iodine compounds are specifically much heavier than the corresponding chlorine compounds.

Bromoform, $CHBr_3$, is obtained by methods analogous to the preparation of chloroform. It melts at 7·8°, boils at 151°, and has a specific gravity of 2·904 at 15°. It is used for therapeutic purposes.

Iodoform, CHI_3.

152. *Iodoform* is a substance of great importance, and is obtained from alcohol by the action of potassium carbonate and iodine. The intermediate product *iodal*, $CI_3{\cdot}CHO$, analogous to chloral, has not been isolated. On the manufacturing scale acetone, being less expensive than alcohol, is often employed.

Iodoform can also be prepared by the electrolysis of a solution containing 60 g. of potassium iodide, 20 g. of sodium carbonate, and 80 c.c. of alcohol per 400 c.c., the temperature being kept between 60° and 65°. Iodine is liberated at the anode, so that the alcohol, potassium carbonate, and iodine necessary to the formation of iodoform are all present in the mixture. By this method about 80 per cent. of the potassium iodide is converted into iodoform, the remainder of the iodine being obtained as potassium iodate. The formation of iodate can be avoided to a great extent by surrounding with parchment the cathode, at which caustic potash is formed: this prevents contact of the potassium carbonate with the iodine set free at the anode.

Iodoform is a solid, and crystallizes in yellow hexagonal plates, well-developed crystals about a centimetre in length being obtained by the slow evaporation of a solution in anhydrous acetone. It has a peculiar, saffron-like odour, sublimes very readily, and melts at 119°.

These characteristic properties of iodoform make its formation an important test for alcohol, although aldehyde, acetone, and several other substances similarly yield iodoform. Substances containing the group $CH_3 \cdot C$ in union with oxygen answer to the *iodoform-test.* It is carried out by adding iodine to the liquid under examination, and then caustic potash drop by drop until the colour of the iodine vanishes. If a considerable quantity of alcohol is present, a yellow precipitate forms at once: if only traces, the precipitate forms after a time. The reaction is sufficiently delicate to show traces of alcohol in a sample of well-water or rain-water, after concentration by repeated distillation, the first fraction in each case being collected.

> Iodoform is employed in surgery as an antiseptic. It is noteworthy that it does not kill the bacteria directly, its action on the micro-organisms being subsequent to a decomposition resulting, under the influence of the heat of the body, from fermentation induced by the matter exuded from the wound.

Methylene iodide, CH_2I_2, is a liquid, and is obtained by the reduction of iodoform with hydriodic acid; phosphorus is added to regenerate the hydriodic acid. Its specific gravity, 3·292 at 18°, is remarkably high.

II. HALOGEN DERIVATIVES OF THE HOMOLOGUES OF METHANE.

153. It is evident that among these derivatives numerous cases of isomerism are possible. For example, replacement by chlorine of three hydrogen atoms in normal pentane may yield several different compounds: thus, a methyl-group may be converted into CCl_3; two chlorine atoms may replace the hydrogen of one methylene-group, while the third replaces another hydrogen atom in the molecule; or the three chlorine atoms may unite with different carbon atoms; and so on.

The preparation of many of the halogen compounds included under this heading has already been described, the compounds $C_nH_{2n+1} \cdot CHX_2$ and $C_pH_{2p+1} \cdot CX_2 \cdot C_qH_{2q+1}$ being obtained by the action of phosphorus pentahalide on aldehydes and ketones respectively (106). Compounds with two halogen atoms attached to two adjoining carbon atoms are obtained by addition of halogen to the hydrocarbons C_nH_{2n}; those having four halogen atoms, two being directly united to each of two adjoining carbon atoms, are produced by addition of halogen to hydrocarbons with a triple bond; while compounds of the type

$$C_pH_{2p+1}\cdot CHX\cdot CHX\cdot C_rH_{2r}\cdot CHX\cdot CHX\cdot C_mH_{2m+1}$$

result on addition of halogen to the hydrocarbons C_nH_{2n-4}, containing two double bonds; etc.

A method for the preparation of compounds rich in halogen from the saturated hydrocarbons is the exchange of one hydrogen atom for halogen, elimination of hydrogen halide by means of alcoholic potash, halogenation of the hydrocarbon C_nH_{2n} thus obtained, removal of HX, renewed halogenation of the product, and so on.

$$\underset{\text{Ethane}}{CH_3\cdot CH_3} \rightarrow \underset{\text{Ethyl chloride}}{CH_3\cdot CH_2Cl} - HCl \rightarrow \underset{\text{Ethylene}}{CH_2{:}CH_2} + 2Cl \rightarrow$$

$$\rightarrow \underset{\text{Ethylene chloride}}{CH_2Cl\cdot CH_2Cl} - 2HCl \rightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 4Cl \rightarrow$$

$$\rightarrow \underset{\text{Tetrachloroethane}}{CHCl_2\cdot CHCl_2} - HCl \rightarrow \underset{\text{Trichloroethylene}}{CHCl{:}CCl_2} + 2Cl \rightarrow$$

$$\rightarrow \underset{\text{Pentachloroethane}}{CHCl_2\cdot CCl_3} - HCl \rightarrow \underset{\text{Tetrachloroethylene}}{CCl_2{:}CCl_2} + 2Cl \rightarrow \underset{\text{Hexachloroethane}}{CCl_3\cdot CCl_3}.$$

A method for the preparation of polybromo-compounds was discovered by VICTOR MEYER, and involves the direct action of bromine on the hydrocarbons of the series C_nH_{2n+2} in presence of a small quantity of anhydrous iron bromide, or iron-wire. These conditions greatly facilitate substitution, each carbon atom of a normal chain taking up only one bromine atom. Thus, propane yields *tribromohydrin*, $CH_2Br\cdot CHBr\cdot CH_2Br$, since the product is identical with the addition-product obtained by the action of bromine on allyl bromide, $CH_2{:}CH\cdot CH_2Br$ (135).

When many of the hydrogen atoms of a hydrocarbon C_nH_{2n+2} have already been replaced by chlorine or bromine, it is no longer possible to substitute hydrogen by the direct action of a halogen: thus, chlorine has no action on pentachloroethane. MOUNEYRAT has, however, found that substitution readily takes place in presence of a small quantity of aluminium chloride, which first splits off hydrogen halides. With aluminium chloride pentachloroethane yields tetrachloroethylene, and the addition of halogen takes place at the double bond thus formed, the product being hexachloroethane.

Nomenclature and Individual Members.

154. The notation adopted by the Chemical Society of London is that "In open-chain compounds Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN, CHO, and CO_2H." Thus, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$ is α-iodobutane; $CH_3 \cdot CH_2 \cdot CH_2 \cdot CN$ α-cyanopropane; $CH_2Br \cdot CH_2 \cdot CH_2Br$ $\alpha\alpha'$-dibromopropane; $CH_2Br \cdot CHBr \cdot CH_3$ $\alpha\beta$-dibromopropane.

Only a few of the numerous compounds of this group will be described.

Ethylene bromide is employed for syntheses and as a solvent. It is prepared by passing ethylene into bromine covered with a layer of water to prevent evaporation, the addition taking place very readily. Ethylene bromide is a colourless liquid of agreeable odour, solidifies at 8°, boils at 131°, and has a specific gravity of 2·189 at 15°.

Ethylene chloride, $CH_2Cl \cdot CH_2Cl$, is called "Dutch Liquid," or the "Oil of the Dutch Chemists," it having been first prepared at the end of the eighteenth century by four Dutch chemists, Deiman, Bondt, Paets van Troostwyk, and Lauwerenburgh, by the action of chlorine upon ethylene. It is a liquid boiling at 84·9°, and has a specific gravity of 1·28 at 0°.

Hexachloroethane (perchloroethane), C_2Cl_6, is formed by the direct union of carbon and chlorine under the influence of a powerful arc-discharge between carbon poles in an atmosphere of chlorine.

Trimethylene bromide, $CH_2Br \cdot CH_2 \cdot CH_2Br$, $\alpha\alpha'$-dibromopropane, also plays an important part in syntheses, and is obtained by addition of HBr to allyl bromide, $CH_2{:}CH \cdot CH_2Br$, produced from allyl alcohol. This method of formation suggests the constitution $CH_3 \cdot CHBr \cdot CH_2Br$, that of the addition-product obtained by the action of bromine upon propylene, $CH_3 \cdot CH{:}CH_2$. Since the two compounds are not identical, trimethylene bromide must have the $\alpha\alpha'$-formula. It is a liquid, boiling at 165°, and has a specific gravity of 1·974 at 17°.

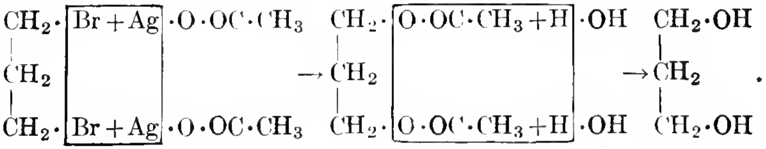
III. POLYHYDRIC ALCOHOLS.

155. When more than one hydrogen atom of a saturated hydrocarbon is replaced by hydroxyl, it is theoretically possible to have more than one hydroxyl-group in union with a single carbon atom, or to have each attached to a different one. It should be possible to obtain compounds of the first class by replacement of halogen by hydroxyl in the halogen derivatives $R \cdot CHX_2$, $R \cdot CX_3$, and $R \cdot CX_2 \cdot R'$. Silver acetate converts halogen compounds of this type into stable acetates, such as $CH_2 < \begin{matrix} OC_2H_3O \\ OC_2H_3O \end{matrix}$. On saponification, however, dihydric alcohols like $CH_2(OH)_2$ are not obtained, but aldehydes result by elimination of one molecule of water. When compounds of the type $RCCl_3$ are treated with sodium ethoxide, substances with the general formula $R \cdot C(OC_2H_5)_3$, called *ortho-esters*, are obtained. On saponification $R \cdot C(OH)_3$ does not result, the corresponding acid being formed instead, through loss of water. Ethers of dihydric alcohols, such as $CH_3 \cdot CH < \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$, are known, and are called *acetals* (113, 2). The saponification of these substances does not yield $R \cdot CH(OH)_2$, but an aldehyde. It follows from these facts that *compounds with more than one hydroxyl-group attached to the same carbon atom are unstable*, although it is sometimes possible to obtain such compounds (201, 249, and 253).

Many compounds are known containing several hydroxyl-groups, of which not more than one is in union with each carbon atom.

1. Glycols or Dihydric Alcohols.

156. The *glycols* are obtained from the corresponding halogen compounds analogously to the monohydric alcohols (43):



Trimethylene bromide

Trimethyleneglycol diacetate

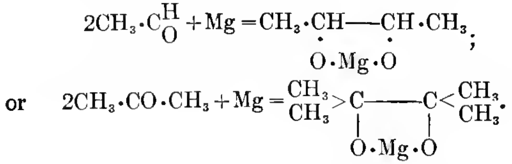
Trimethyleneglycol

The exchange of halogen for hydroxyl can be brought about by treatment with acetate of silver or the acetate of an alkali-metal, and saponification of the diacetate thus obtained. It can also be effected directly by boiling with sodium-carbonate solution, or water and lead oxide.

Glycols of the type R·CHOH·CHOH·R, with the CHOH-groups in direct union, are formed from olefines either through the medium of their bromine addition-products, or by the direct addition of two OH-groups by means of careful oxidation with potassium permanganate. Thus, ethylene yields the simplest dihydric alcohol, called *glycol:*

$$\mathrm{CH_2{:}CH_2 + H_2O + O = CH_2OH\cdot CH_2OH.}$$

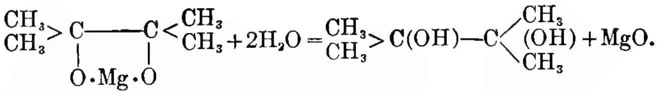
Another method for the formation of glycols of this type consists in the reduction of ketones. This may be either carried out with sodium in aqueous solution, or by electrolysis. Acetone yields *pinacone* and *iso*propyl alcohol. Glycols of the type of pinacone—called *pinacones*—can be obtained without admixture of a secondary alcohol by reduction of aldehydes or ketones with magnesium-amalgam, addition-products being first formed with evolution of heat:



$$\mathrm{2CH_3\cdot C{\begin{smallmatrix}H\\O\end{smallmatrix}} + Mg = \begin{array}{c}CH_3\cdot CH—CH\cdot CH_3\\ O\cdot Mg\cdot O\end{array};}$$

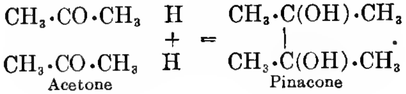
$$\text{or}\quad \mathrm{2CH_3\cdot CO\cdot CH_3 + Mg = \begin{array}{c}{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}>C——C<{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}\\ \mid\qquad\mid\\ O\cdot Mg\cdot O\end{array}.}$$

Water decomposes the addition-product, with formation of the pinacone:



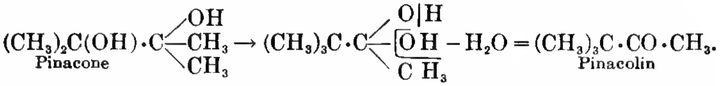
$$\mathrm{\begin{array}{c}{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}>C——C<{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}\\ \mid\qquad\mid\\ O\cdot Mg\cdot O\end{array} + 2H_2O = {\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}>C(OH)—C{\begin{smallmatrix}CH_3\\(OH)\\CH_3\end{smallmatrix}} + MgO.}$$

The constitution of pinacone is indicated by its synthesis:



$$\mathrm{\underset{\text{Acetone}}{\begin{array}{c}CH_3\cdot CO\cdot CH_3\\ \\ CH_3\cdot CO\cdot CH_3\end{array}}\ \begin{array}{c}H\\+\\H\end{array} = \underset{\text{Pinacone}}{\begin{array}{c}CH_3\cdot C(OH)\cdot CH_3\\ \mid\\ CH_3\cdot C(OH)\cdot CH_3\end{array}}.}$$

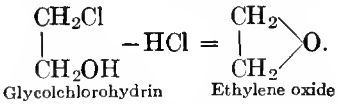
When distilled with dilute sulphuric acid, pinacone undergoes a remarkable intramolecular transformation, explicable on the assumption that a hydroxyl-group changes place with a methyl-group:



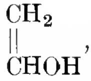
$$\underset{\text{Pinacone}}{(CH_3)_2C(OH)\cdot C}\begin{array}{l}\diagup OH\\ -CH_3\\ \diagdown CH_3\end{array} \rightarrow (CH_3)_3C\cdot C\begin{array}{l}\diagup O|H\\ -\boxed{O\,H}\\ \diagdown C\,H_3\end{array} - H_2O = \underset{\text{Pinacolin}}{(CH_3)_3C\cdot CO\cdot CH_3.}$$

The constitution of *pinacolin* may be deduced from its synthesis by the action of zinc methide on trimethylacetyl chloride, $(CH_3)_3C\cdot COCl$, and in other ways.

Most of the glycols are colourless, viscous liquids of sweet taste, whence the series derives its name. Their boiling-points and specific gravities are considerably higher than those of the monohydric alcohols with the same number of carbon atoms. Thus, glycol boils at 197·5°, and ethyl alcohol at 78°: at 0° the specific gravity of glycol is 1·128, and of ethyl alcohol 0·806. The nature of the hydroxyl-groups in glycol and that in the monohydric alcohols is perfectly analogous: exchange of OH for halogen, the formation of ethers, esters, and alkoxides, and the oxidation of primary glycols to aldehydes and acids, may take place in connection with one or both of the hydroxyl-groups. For instance, the compounds $CH_2OH\cdot CH_2Cl$, *glycolchlorohydrin;* $CH_2OC_2H_5\cdot CH_2OH$, *glycol-monoethyl ether;* $CH_2OC_2H_5\cdot CH_2OC_2H_5$, *glycol diethyl ether;* etc.; are known. The glycols possess, however, one property due to the presence of two hydroxyl-groups, the power of forming anhydrides. The first member of the series, glycol, $CH_2OH\cdot CH_2OH$, does not yield an anhydride by the direct elimination of water, but a compound of the formula C_2H_4O is obtained by first replacing one hydroxyl-group by Cl and then eliminating HCl:



$$\underset{\text{Glycolchlorohydrin}}{\begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array}} - HCl = \underset{\text{Ethylene oxide}}{\begin{array}{l}CH_2\diagdown\\ |\qquad\rangle O.\\ CH_2\diagup\end{array}}$$

This compound, *ethylene oxide*, boils at 14°, and is therefore gaseous at ordinary temperatures: it readily takes up water, forming glycol; or hydrochloric acid, forming glycolchlorohydrin. To ethylene oxide is assigned the constitutional formula indicated, because it yields ethylene chloride when treated with phosphorus pentachloride, the oxygen atom being replaced by two chlorine atoms. If the compound had the constitution  $\begin{array}{l}CH_2\\ \|\\ CHOH\end{array}$, which is also possible but less probable (136), it would not yield ethylene chloride when thus treated.

Some of the higher homologues of glycol with a chain of four or five carbon atoms between the hydroxyl-groups yield anhydrides with a constitution analogous to that of ethylene oxide. They show a marked diminution in the power of forming addition-products with water; or, in other words, the *closed chain* of carbon atoms and one oxygen atom is more stable than in ethylene oxide itself.

2. Trihydric Alcohols.

157. The principal representative of the group of trihydric alcohols is *glycerol*, or "glycerine," $C_3H_5(OH)_3$. In accordance with the rule that two hydroxyl-groups cannot attach themselves to the same carbon atom, glycerol can only have the structure

$$CH_2OH \cdot CHOH \cdot CH_2OH.$$

This structure finds support in other proofs.

1. On careful oxidation of allyl alcohol by means of potassium permanganate, two OH-groups are added at the position of the double bond:

$$CH_2{:}CH \cdot CH_2OH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH.$$

2. When glycerol, $C_3H_8O_3$, is carefully oxidized, *glyceric acid*, $C_3H_6O_4$, is first formed, corresponding to the formation of acetic acid, $C_2H_4O_2$, from ethyl alcohol, C_2H_6O, by exchange of two hydrogen atoms for one oxygen atom: this indicates that glycerol contains one $-CH_2OH$-group. Further oxidation converts glyceric acid into *tartronic acid*, $C_3H_4O_5$, two hydrogen atoms being replaced by one oxygen atom, with formation of a new carboxyl-group. Hence, glycerol contains two $-CH_2OH$-groups in the molecule, so that its constitution is $CH_2OH \cdot CH_2O \cdot CH_2OH$. Since tartronic acid, $COOH \cdot CH_2O \cdot COOH$, still possesses alcoholic properties, the group CH_2O must have the constitution $>CHOH$,

and since it must have the same constitution in the molecule of glycerol, the structure of the latter is proved to be $CH_2OH \cdot CHOH \cdot CH_2OH$.

3. A further proof of the constitution given above is the formation of glycerol from tribromohydrin (153).

Glycerol is a colourless, oily liquid of sweet taste, is very hygroscopic, and miscible in all proportions with water and alcohol, but insoluble in ether. When cooled to a low temperature for some time, it solidifies, but the crystals thus formed do not melt below 17°. It boils at 290°, and has a specific gravity of 1·265 at 15°. Its chemical behaviour accords completely with the constitution of a trihydric alcohol. Thus, it yields three esters, by replacement of one, two, or three hydroxyl-groups. When borax is dissolved in glycerol or in a solution of this substance and the mixture introduced into the flame, the green colour characteristic of free boric acid is observed: on this reaction is based **Senier**'s test for glycerol.

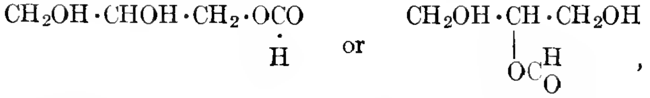
Since glycerol is a substance which plays a very important part in the economy of nature as a constituent of the fats (159), its synthesis from its elements is of great interest. This was effected by **Friedel** and **Silva**, the starting-point being acetic acid. This substance can be synthesized from its elements in several ways, for example by the oxidation of acetaldehyde obtained by the action of water on acetylene (132). The dry distillation of calcium acetate gave acetone, which was reduced to *iso*propyl alcohol. On elimination of water from this alcohol, propylene was formed, and on addition of chlorine, was converted into propylene chloride, from which trichlorohydrin was obtained by treatment with iodine chloride. Trichlorohydrin was converted into glycerol by heating with water at 170°:

$$\underset{\text{Acetic acid}}{CH_3 \cdot COOH} \rightarrow \underset{\text{Acetone}}{CH_3 \cdot CO \cdot CH_3} \rightarrow \underset{\textit{iso}\text{Propyl alcohol}}{CH_3 \cdot CHOH \cdot CH_3} \rightarrow \underset{\text{Propylene}}{CH_3 \cdot CH : CH_2} \rightarrow$$

$$\rightarrow \underset{\text{Propylene chloride}}{CH_3 \cdot CHCl \cdot CH_2Cl} \rightarrow \underset{\text{Trichlorohydrin}}{CH_2Cl \cdot CHCl \cdot CH_2Cl} \rightarrow \underset{\text{Glycerol}}{CH_2OH \cdot CHOH \cdot CH_2OH}.$$

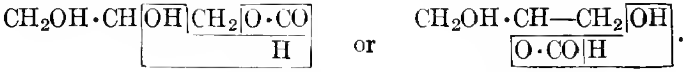
158. Several compounds, difficult to prepare otherwise, can be obtained from glycerol. Among them are allyl alcohol, allyl iodide, acroleïn, and *iso*propyl iodide.

Allyl alcohol, $CH_2 : CH \cdot CH_2OH$, can be prepared from glycerol by heating it with oxalic acid, $COOH\cdot COOH$. *Glyceryl monoformate* or *monoformin*,



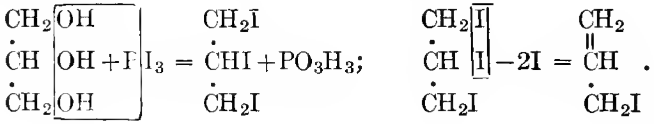
$$CH_2OH\cdot CHOH\cdot CH_2\cdot O\underset{\substack{\cdot\\ H}}{C}O \quad \text{or} \quad CH_2OH\cdot \underset{\substack{| \\ OC\substack{H\\ O}}}{CH}\cdot CH_2OH,$$

is first produced, as under these conditions oxalic acid loses one molecule of carbon dioxide, yielding formic acid, $\boxed{COO}H—COOH$, which combines with the glycerol to produce monoformin. When heated more strongly, this decomposes into allyl alcohol, water, and carbon dioxide:



$$CH_2OH\cdot CH\boxed{\begin{array}{l} OH\,|\,CH_2\,|\,O\cdot CO \\ \hfill H \end{array}} \quad \text{or} \quad \begin{array}{l} CH_2OH\cdot CH—CH_2\boxed{OH} \\ \qquad\qquad\;\; \boxed{O\cdot CO\,|\,H} \end{array}.$$

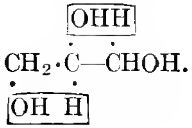
Allyl iodide is obtained by the action of phosphorus and iodine on anhydrous glycerol:



$$\begin{array}{l} CH_2\boxed{OH} \\ \overset{\bullet}{C}H\;\;\boxed{OH}+P\,|\,I_3 \\ \overset{\bullet}{C}H_2\boxed{OH} \end{array} = \begin{array}{l} CH_2I \\ \overset{\bullet}{C}HI+PO_3H_3; \\ \overset{\bullet}{C}H_2I \end{array} \qquad \begin{array}{l} CH_2\boxed{I} \\ \overset{\bullet}{C}H\;\boxed{I}-2I \\ \overset{\bullet}{C}H_2I \end{array} = \begin{array}{l} CH_2 \\ \overset{\|}{C}H\;. \\ \overset{\bullet}{C}H_2I \end{array}$$

The tri-iodohydrin, $C_3H_5I_3$, probably formed as an intermediate product in this reaction is unstable, and at once loses two atoms of iodine, yielding allyl iodide.

Acroleïn (147) results by elimination of water from glycerol:



$$\begin{array}{c} \boxed{OHH} \\ CH_2\cdot \overset{\bullet}{C}—\overset{\bullet}{C}HOH. \\ \boxed{OH\;\;H} \end{array}$$

$CH_2{:}C{:}CHOH$ should be obtained, but immediately changes to acroleïn, $CH_2{:}CH\cdot C\substack{H\\ O}$ (136).

iso*Propyl iodide* is formed by the addition of water to a mixture of glycerol with iodine and phosphorus. In this reaction. propylene, $CH_3\cdot CH{:}CH_2$, is an intermediate product, and is evolved in the free state if insufficient hydriodic acid is present.

By the addition of HI, produced by the interaction of iodine, phosphorus, and water, *iso*propyl iodide is formed from the propylene thus generated:

$$\underset{\text{Propylene}}{CH_3\cdot CH{:}CH_2} + HI = \underset{\textit{iso}\text{Propyl iodide}}{CH_3\cdot CHI\cdot CH_3}.$$

Formic acid (**88**) is usually prepared by the action of glycerol on oxalic acid. As previously mentioned, when these substances are heated together, carbon dioxide is evolved, and glyceryl monoformate produced. Formic acid is obtained from the latter by saponification, the glycerol being simultaneously regenerated by the addition of a fresh quantity of oxalic acid, $C_2H_2O_4\cdot 2aq$, the water of crystallization saponifying the ester, and the formic acid distilling over. The glycerol thus regenerated is again converted into monoformin by the freshly-added oxalic acid, and the ester once more decomposed by the addition of a further quantity of oxalic acid, and so on. It is thus possible to convert unlimited quantities of oxalic acid into formic acid by means of a given quantity of glycerol.

159. Glycerol occurs in nature in large quantities in the form of esters. The fats and oils are glyceryl tri-esters of the higher fatty acids and of oleïc acid: glycerol and the fatty acids are obtained from them by saponification (**91** and **101**).

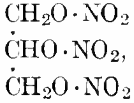
Saponification of the esters of polyhydric alcohols.—The saponification of the tri-esters of glycerol with caustic soda or lime takes place in stages, the di-esters and mono-esters being formed as intermediate products, as can be readily proved. On complete saponification, pure tristearin, or glyceryl tristearate yields only stearic acid and glycerol, so that if no intermediate products are formed, a partially-saponified portion, in which the soap produced has been decomposed by hydrochloric acid, and the glycerol removed by washing with water, should contain only unchanged tristearin and stearic acid. Neither tristearin nor stearic acid can yield acetyl-derivatives with acetic anhydride. If the saponification takes place in stages, monostearin and distearin should be formed, and the free hydroxyl-groups of the glyceryl-residue in these compounds should react with acetic anhydride to form acetyl-compounds. On treatment with this anhydride, and subsequent complete saponification, acetic acid should be among the products, and it has been proved by experiment that this is so.

When glycol diacetate and glyceryl diacetate are saponified with very dilute hydrochloric acid, the velocity of saponification for each compound differs at the various stages. It has been stated that the ratio of the velocity-constant of glycol diacetate to that of the monoacetate is as 2:1, the corresponding ratio for the glyceryl tri-esters, di-esters, and mono-esters being as 3:2:1. It is obvious that during saponification a molecule containing n acid-radicals will encounter the hydroxyl-ions or hydrogen ions n times as often as if only one were present. It follows that in the saponification of poly-esters, the ratio of the velocity-constants of the individual stages must correspond with that of the acid-radicals present in each stage.

Inversely, the fats can be synthesized from glycerol and the fatty acids: for instance, tristearin is obtained by heating glycerol with excess of stearic acid under reduced pressure at 200° until separation of water ceases.

Many fats gradually become *rancid*, and develop a disagreeable smell and taste. This is due to atmospheric oxidation, which is facilitated by the influence of light. The unsaturated fatty acids become converted into others containing a smaller number of carbon atoms, and with a characteristic odour and taste.

160. Glycerol is extensively employed in the arts and in medicine. One of its most important applications is to the preparation of the so-called "nitroglycerine." This explosive has a misleading name, since it is glyceryl trinitrate,



$$\begin{array}{l} CH_2O\cdot NO_2 \\ \dot{C}HO\cdot NO_2, \\ \dot{C}H_2O\cdot NO_2 \end{array}$$

and not a nitro-compound (75); for on saponification with alkalis it yields glycerol, and the nitrate of the corresponding alkali-metal.

Nitroglycerine is prepared by bringing glycerol into contact with a mixture of concentrated sulphuric acid and nitric acid, rise of temperature being prevented. After a time, the reaction-mixture is poured into water, whereupon the nitrate separates in the form of an oily, very explosive liquid of faint, headache-producing odour. It can be purified by washing with water, and when perfectly pure does not explode spontaneously.

Nitroglycerine is a liquid, and as its use in this form for technical purposes would be attended with difficulties, it is mixed with infusorial earth ("kieselguhr"), which absorbs it, forming a soft, plastic mass, *dynamite*, containing usually 75 per cent. of nitroglycerine and 25 per cent. of the earth. Nitroglycerine can also be obtained in the solid form by dissolving in it a small amount of guncotton (**228**), which converts it into an elastic solid resembling jujubes in consistence, called "blasting gelatine." This substance has the advantage over dynamite of not leaving any solid residue after explosion. Dynamite cannot be used as ammunition, its velocity of explosion being so great as to produce an impulse too violent for a gun to resist without bursting: that is, it exerts a "brisant" or detonating effect.

3. Tetrahydric and Polyhydric Alcohols.

161. Among the tetrahydric alcohols is *erythritol,*

$$CH_2OH \cdot CHOH \cdot CHOH \cdot CH_2OH,$$

which is a natural product. It contains a normal carbon chain, since reduction with hydriodic acid converts it into *n*-secondary butyl iodide, $CH_3 \cdot CHI \cdot CH_2 \cdot CH_3$.

Examples of pentahydric alcohols are *arabitol and xylitol,* $C_5H_{12}O_5$, which are stereoisomerides, as are also the hexahydric alcohols *dulcitol and mannitol,* $C_6H_{14}O_6$, both of which are found in nature. These all have normal carbon chains, since, like erythritol, they yield *n*-secondary iodides on reduction with hydriodic acid: thus, mannitol is converted into

$$CH_3 \cdot CH_2 \cdot CHI \cdot CH_2 \cdot CH_2 \cdot CH_3.$$

They can be obtained artificially by the reduction of the corresponding aldehydes or ketones. The reason for assuming their stereoisomerism is explained in **209**, but here it may be pointed out that the polyhydric alcohols contain asymmetric carbon atoms, indicated in the formulæ by asterisks:

$$CH_2OH \cdot \overset{*}{C}HOH \cdot CHOH \cdot \overset{*}{C}HOH \cdot CH_2OH;$$

Arabitol and Xylitol

$$CH_2OH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot CH_2OH.$$

Dulcitol and Mannitol

The presence of polyhydric alcohols prevents the precipitation of the hydroxides of copper, iron, and other metals by means of alkalis. Thus, a solution of copper sulphate and glycerol does not yield a precipitate of copper hydroxide with caustic potash. This is due to the formation of soluble metallic compounds of the polyhydric alcohols, the hydroxyl-hydrogen being replaced by the metal. The acidic nature of the hydroxyl-group, almost lacking in the monohydric alcohols, is therefore in some measure developed by increase in the number of these groups present in the molecule. This property is possessed not only by the polyhydric alcohols, but also by many other compounds containing several hydroxyl-groups (192).

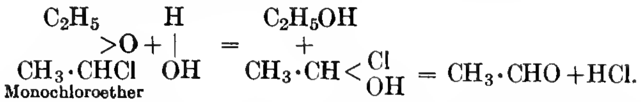
IV. DERIVATIVES CONTAINING HALOGEN ATOMS, HYDROXYL-GROUPS, NITRO-GROUPS, OR AMINO-GROUPS.

162. Only a few of the numerous compounds belonging to this class will be considered: the chemical properties of its members are determined by the substituents.

No compounds containing halogen and hydroxyl in union with the same carbon atom are known: when their formation might be expected, hydrogen halide is eliminated, with production of aldehydes or ketones. It has been mentioned more than once that stable alkyl-derivatives of compounds themselves unstable or unknown, such as the ortho-esters, exist (155). This is true in this instance, for while compounds of the type $R\cdot CH<^{Cl}_{OH}$ are unknown, derivatives of the formula $R\cdot CH<^{Cl}_{O\cdot C_nH_{2n+1}}$ are known. These substances are called *chloroethers*. When chlorine is passed into ethyl ether, kept cool and in the dark to avoid explosion, the hydrogen atoms are replaced by chlorine. The monosubstitution-product has the constitution

$$\underset{\text{Monochloroether}}{CH_3\cdot CH_2\cdot O\cdot CHCl\cdot CH_3},$$

as is proved by the action of sulphuric acid, under the influence of which it takes up one molecule of water, forming ethyl alcohol, acetaldehyde, and hydrochloric acid:



$$\underset{\text{Monochloroether}}{\begin{matrix}C_2H_5\\ \quad >O\\ CH_3\cdot CHCl\end{matrix}} + \begin{matrix}H\\ |\\ OH\end{matrix} = \begin{matrix}C_2H_5OH\\ +\\ CH_3\cdot CH<\begin{matrix}Cl\\ OH\end{matrix}\end{matrix} = CH_3\cdot CHO + HCl.$$

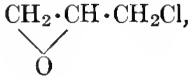
Compounds containing halogen and hydroxyl in union with different carbon atoms are obtained from the polyhydric alcohols by partial exchange of hydroxyl for halogen, and have the general name *halogen-hydrins*. *Glycerol dichlorohydrin*, $C_3H_5(OH)Cl_2$, is formed when a solution of glycerol in glacial acetic acid is saturated with hydrochloric-acid gas. It has the symmetrical formula

$$CH_2Cl\cdot CHOH\cdot CH_2Cl,$$

since it differs from the dichlorohydrin obtained by addition of chlorine to allyl alcohol, this having the constitution

$$CH_2OH\cdot CHCl\cdot CH_2Cl.$$

On treatment of both dichlorohydrins with caustic potash, *epichlorohydrin*,



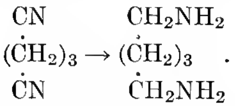
is obtained.

Dinitro-compounds with both nitro-groups in union with the same carbon atom are formed from primary bromo-nitro-compounds by the action of potassium nitrite:

$$CH_3\cdot CHBrNO_2 + KNO_2 = CH_3\cdot CH(NO_2)_2 + KBr.$$

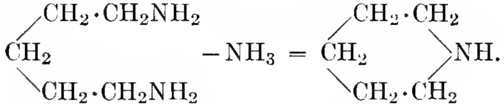
The hydrogen atom belonging to the carbon atom carrying the nitro-groups can be readily replaced by metals, so that these primary dinitro-compounds have an acidic character (311).

Diamines with the two amino-groups attached to the same carbon atom are not numerous: most of them have their amino-groups in union with different carbon atoms. Some of these compounds are formed by the putrefaction of animal matter, such as flesh, and are classed as *ptomaïnes* with other basic substances similarly formed. Such are *cadaverine* (*pentamethylenediamine*), $NH_2\cdot CH_2\cdot (CH_2)_3\cdot CH_2\cdot NH_2$, and *putrescine* (*tetramethylenediamine*), $NH_2\cdot CH_2\cdot (CH_2)_2\cdot CH_2\cdot NH_2$. The constitution of these substances has been proved by synthesis, pentamethylenediamine being thus obtained. Trimethylene bromide, $Br \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot Br$, is converted by treatment with potassium cyanide into trimethylene cyanide, $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CN$. This substance is reduced with sodium and boiling alcohol, which converts the CN-groups into CH_2NH_2-groups (85), with formation of the diamine:



$$\begin{matrix} CN & & CH_2NH_2 \\ \dot{(CH_2)_3} & \rightarrow & \dot{(CH_2)_3} \\ \dot{CN} & & \dot{CH_2NH_2} \end{matrix} .$$

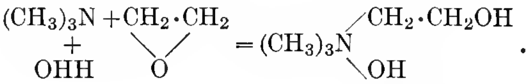
When pentamethylenediamine hydrochloride is heated, it loses one molecule of ammonia, and is converted into *piperidine*, which has the character of a saturated secondary amine. For this and other reasons (450) it is assigned a ring or cyclic formula:



Pentamethylenediamine Piperidine

When heated, tetramethylenediamine and trimethylenediamine yield analogous cyclic compounds, but less readily, whereas ethylenediamine does not.

A substance, partly amine and partly alcohol, should be mentioned on account of its physiological importance: it is *choline*, $C_5H_{15}O_2N$, which is widely distributed in the vegetable kingdom. Its constitution is inferred from its synthesis by the interaction of trimethylamine and ethylene oxide in aqueous solution:



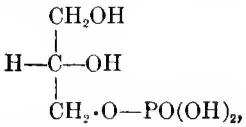
Choline

Ethylene oxide can also combine with substances like ethylamine, with formation of amino-alcohols.

Choline is a constituent of a very complicated compound, *lecithin*, present in brain-substance, yolk of egg, many seeds, and elsewhere. It is glycerophosphoric acid in which the alcoholic hydroxyl-groups are esterified by palmitic, stearic, and oleïc acid;

and the acidic hydroxyl-groups are combined with choline. Various lecithins are known: some of them probably contain more than one kind of acid-residue in the molecule. The native lecithins are always mixtures.

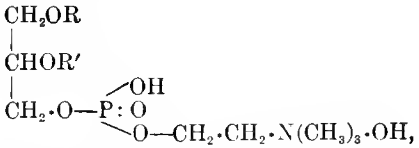
On treatment with baryta-water, lecithin yields choline, one or more of the fatty acids named above, and glycerophosphoric acid. This acid is optically active, and has the formula



$$\begin{array}{l} CH_2OH \\ \;| \\ H—C—OH \\ \;| \\ CH_2\cdot O—PO(OH)_2, \end{array}$$

the central C-atom being asymmetric.

Lecithin, likewise, is optically active, and may have the formula



R and R′ being similar or dissimilar acid-radicals.

The lecithins dissolve readily in alcohol, but with difficulty in ether. As the structural formula indicates, they yield salts with both bases and acids.

POLYBASIC ACIDS.

I. SATURATED DIBASIC ACIDS, $C_nH_{2n-2}O_4$.

163. Many isomerides of the acids $C_nH_{2n}(COOH)_2$ are theoretically possible, and differ from one another in the positions at which the carboxyl-groups are linked to the carbon chain. For many reasons, the most important are those with carboxyl-groups attached to the terminal carbon atoms of the normal chain, the $\alpha\alpha'$-acids (154).

The general methods for the preparation of the dibasic acids and the monobasic acids are analogous. The former are produced by the oxidation of the corresponding glycols and aldehydes, and by the hydrolysis of the dinitriles, although many of them are prepared by special methods.

Physical and Chemical Properties.

164. These acids are well-defined crystalline substances: those with more than three carbon atoms can be distilled *in vacuo* without decomposition. When distilled under ordinary pressure, many of them lose water.

The melting-points of these acids exhibit the same peculiarity as those of the fatty acids (87): the members with an even number of carbon atoms have higher melting-points than those immediately succeeding them, with an uneven number of carbon atoms, as is seen from the table on next page.

This relation is graphically represented in Fig. 32, which indicates that the melting-points of the even and uneven series approximate more and more closely as the number of the carbon atoms increases.

A similar peculiarity is displayed by other physical constants of these acids, that of the solubility in water being given in the last column of the table. The solubility of the acids with an uneven number of carbon atoms is much greater than the solubility of those with an even number, and for both it diminishes with increase in the number of carbon atoms.

Name.	Formula.	Melting-point.	Parts by Weight Soluble in 100 Part of Water.
Oxalic acid.	$\mathrm{COOH\cdot COOH}$	189° *	10·2 at 20°
Malonic acid.	$\mathrm{COOH\cdot CH_2\cdot COOH}$	132°	139·37 '' 15°
Succinic acid.	$\mathrm{COOH\cdot (CH_2)_2\cdot COOH}$	182°	5·14 '' 14·5°
Glutaric acid.	$\mathrm{COOH\cdot (CH_2)_3\cdot COOH}$	98°	80·3 '' 14°
Adipic acid.	$\mathrm{COOH\cdot (CH_2)_4\cdot COOH}$	153°	1·44 '' 15°
Pimelic acid.	$\mathrm{COOH\cdot (CH_2)_5\cdot COOH}$	105·5°	4·1 '' 20°
Suberic acid.	$\mathrm{COOH\cdot (CH_2)_6\cdot COOH}$	141°	0·142'' 15·5°
Azelaïc acid.	$\mathrm{COOH\cdot (CH_2)_7\cdot COOH}$	108°	
Sebacic acid.	$\mathrm{COOH\cdot (CH_2)_8\cdot COOH}$	134·5°	0·1 '' 17°
Nonanedicarboxylic acid.	$\mathrm{COOH\cdot (CH_2)_9\cdot COOH}$	110°	
Decamethylene-dicarboxylic acid.	$\mathrm{COOH\cdot (CH_2)_{10}\cdot COOH}$	125°	
Brassylic acid.	$\mathrm{COOH\cdot (CH_2)_{11}\cdot COOH}$	112°	
Dodecamethylene-dicarboxylic acid. .	$\mathrm{COOH\cdot (CH_2)_{12}\cdot COOH}$	123°	

* Anhydrous oxalic acid.

Oxalic acid is a very much stronger acid than its homologues, as the dissociation-constants indicate. For oxalic acid 10^4k is about 1000, for malonic acid 16·3, and for succinic acid 0·65: for the remaining acids it has values which diminish with increase in

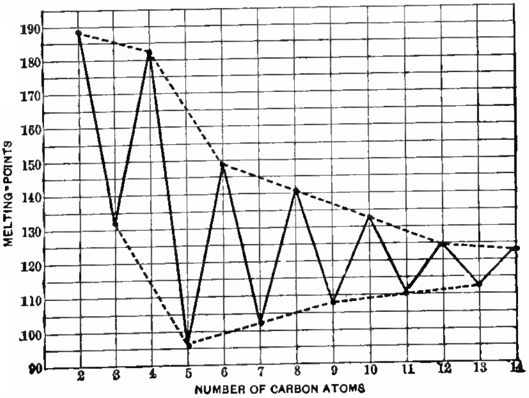
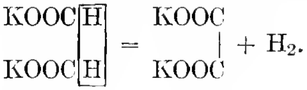


FIG. 32.—GRAPHIC REPRESENTATION OF THE MELTING-POINTS OF THE ACIDS $C_nH_{2n-2}O_4$.

the number of carbon atoms, but are of the same order as the last number. The longer the carbon chain between the carboxyl-groups, the weaker is the acid (172).

Oxalic Acid, $C_2H_2O_4 + 2H_2O$.

165. Between *oxalic acid* and formic acid there exists a genetic interdependence: it is possible to prepare formic acid from oxalic, or conversely, oxalic from formic acid. On rapidly heating potassium or sodium formate, hydrogen is evolved from the fusing mass, and potassium or sodium oxalate is produced:



$$\begin{array}{l}\mathrm{KOOC}\boxed{\mathrm{H}}\\ \\ \mathrm{KOOC}\boxed{\mathrm{H}}\end{array} = \begin{array}{r}\mathrm{KOOC}\\ |\\ \mathrm{KOOC}\end{array} + H_2.$$

The reverse transformation of oxalic acid into formic acid has already been described (158), and constitutes the ordinary method for the preparation of formic acid.

Oxalic acid frequently results in the oxidation of organic substances with nitric acid: thus, it is formed by the action of this acid on sugar. It is prepared on the manufacturing scale by heating a mixture of caustic potash and caustic soda to the point of fusion along with sawdust. A formate is an intermediate product, and on further heating loses hydrogen, being converted into an oxalate. After cooling, the mass is lixiviated with water, the oxalate going into solution: the oxalic acid is then precipitated as calcium oxalate by the addition of milk of lime, and finally obtained in the free state by the action of sulphuric acid.

The production of this acid by the interaction of carbon dioxide and potassium or sodium at about 360°, and its formation by the hydrolysis of cyanogen, $CN \cdot CN$, are of theoretical importance.

Oxalic acid occurs in nature in different plants, chiefly in species of *oxalis*, in the form of potassium hydrogen, or calcium, salt. It is sometimes found as a crystalline deposit of calcium oxalate in plant-cells. It crystallizes with two molecules of water of crystallization, which it begins to lose at 30°. On careful heating the anhydrous acid sublimes, but when strongly heated, either alone or with concentrated sulphuric acid, it decomposes into CO_2, CO, and H_2O. A similar decomposition ensues when a solution of uranium oxalate is exposed to sunlight, CO and CO_2 being energetically evolved. Oxalic acid is very readily oxidized: a volumetric method for its estimation depends upon the use of potassium permanganate in sulphuric-acid solution, each molecule of oxalic acid requiring one atom of oxygen:

$$C_2H_2O_4+O = 2CO_2+H_2O.$$

The oxidation with permanganate accords with the equation

$$2KMnO_4+5C_2H_2O_4+3H_2SO_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O.$$

The manganese sulphate formed has a catalytic accelerating action on the process, so that, although the first few drops of permanganate solution are very slowly decolorized, after further addition of permanganate the disappearance of the colour is instantaneous. When manganese sulphate is added to the oxalic-acid solution before the titration, the permanganate is at once decolorized.

Only the salts of the alkali-metals are soluble in water. Calcium oxalate, $CaC_2O_4,2aq$, is insoluble in acetic acid, but soluble in mineral acids ("Inorganic Chemistry," 259): its formation serves as a test both for calcium and for oxalic acid. As a dibasic acid, oxalic acid yields both acid and normal salts, and the so-called *quadroxalates* are known—compounds of one molecule of acid salt with one molecule of acid: among these is "salt of sorrel," $KHC_2O_4+H_2C_2O_4+2aq$. A great number of complex salts of oxalic acid are known: many of them contain alkali-metals, and are soluble in water. They are employed in electro-analysis.

A type of these complex salts is *potassium ferrous oxalate*, $K_2Fe(C_2O_4)_2$, which yields a yellow solution. This indicates the presence of a complex ion, probably $(Fe(C_2O_4)_2)''$, since ferrous salts are usually light-green. Potassium ferrous oxalate is a strong reducing agent: it is employed for the development of photographic plates.

Potassium ferric oxalate, $K_3Fe(C_2O_4)_3$, yields a green solution, which must, therefore, also contain a complex ion, possibly $(Fe(C_2O_4)_3)'''$. Its solution is rapidly reduced by sunlight, in accordance with the equation

$$2K_3Fe(C_2O_4)_3 = 2K_2Fe(C_2O_4)_2+K_2C_2O_4+2CO_2.$$

This property is made use of in the preparation of *platinotypes*. The photographic negative is placed upon a sheet of paper saturated with potassium ferric oxalate: reduction to ferrous salt only takes place where the light is transmitted through the negative, and when the paper is placed in a solution of a platinum salt, the metal is only deposited on the parts coated with potassium ferrous oxalate.

Dimethyl oxalate is solid, and melts at 54°: it is employed in the preparation of pure methyl alcohol. *Diethyl oxalate* is a liquid. Both are prepared by distilling a solution of anhydrous oxalic acid in the absolute alcohol.

Oxalyl chloride, $COCl \cdot COCl$, is prepared by the interaction of two gramme-molecules of phosphorous pentachloride and one gramme-molecule of oxalic acid. It is a colourless liquid, boils at 64°, and at $-12°$ solidifies to white crystals. When its vapour is brought into contact with steam, oxalic acid and hydrochloric acid are formed. Liquid water, however, converts it quantitatively into carbon dioxide, carbon monoxide, and hydrochloric acid.

Oxamide, $CONH_2 \cdot CONH_2$, is a white solid, nearly insoluble in water, alcohol, and ether, and is obtained as a crystalline precipitate by the addition of ammonia to a solution of a dialkyl oxalate. The monoamides of the dibasic acids are called *amic acids*, that of oxalic acid being *oxamic acid*, $CONH_2 \cdot COOH$. It is a crystalline compound, readily soluble in cold water, and insoluble in alcohol.

Malonic Acid, $COOH \cdot CH_2 \cdot COOH$.

166. The constitution of *malonic acid* is proved by its synthesis from monochloroacetic acid. When an aqueous solution of potassium monochloroacetate is boiled with potassium cyanide, cyanoacetic acid is formed, and can be converted into malonic acid by hydrolysis of the nitrile-group:

$$CH_2{<}\begin{matrix}Cl\\COOH\end{matrix} \rightarrow CH_2{<}\begin{matrix}CN\\COOH\end{matrix} \rightarrow CH_2{<}\begin{matrix}COOH\\COOH\end{matrix}.$$

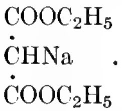
Monochloroacetic acid Cyanoacetic acid Malonic acid

Malonic acid is a crystalline substance: some of its physical properties are given in the table in **164**. When heated somewhat above its melting-point, it loses one molecule of carbon monoxide, being converted into acetic acid:

$$COOH \cdot CH_2 \cdot \boxed{COO}H = CO_2 + COOH \cdot CH_3.$$

It is found that *when a compound with two carboxyl-groups in union with one carbon atom is heated above its melting-point, its molecule loses one molecule of carbon dioxide.*

The most important derivative of malonic acid is *diethyl malonate*, many important syntheses being accomplished by its aid. It is a liquid of faint odour, boiling at 198°, and having a specific gravity of 1·061 at 15°. On treatment with sodium, in the proportion of one atom to each molecule of ester, hydrogen is evolved, and the diethyl malonate converted into a solid mass. In this reaction, hydrogen is replaced by sodium, yielding *diethyl monosodiomalonate*, a compound of the structure



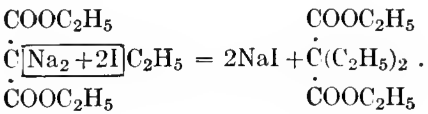
$$\begin{array}{l}COOC_2H_5\\ \dot{C}HNa\\ \dot{C}OOC_2H_5\end{array}.$$

This is proved by treating it with an alkyl halide (iodide), a sodium halide and an ester being obtained:

$$C_2H_5\boxed{I+Na}CH(COOC_2H_5)_2 = C_2H_5{\cdot}CH(COOC_2H_5)_2+NaI.$$

On saponification, this ester yields a homologue of malonic acid.

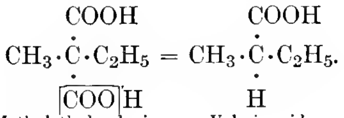
If two atoms of sodium, instead of one, react with one molecule of diethyl malonate, two hydrogen atoms are replaced. Both of these hydrogen atoms are in the methylene-group, because, on treatment of the disodio-compound with two molecules of an alkyl iodide, the two sodium atoms are replaced by alkyl, with production of a substance which on saponification is converted into a homologue of malonic acid:



$$\begin{array}{l}COOC_2H_5\\ \dot{C}\boxed{Na_2+2I}C_2H_5\\ \dot{C}OOC_2H_5\end{array} = 2NaI+\begin{array}{l}COOC_2H_5\\ \dot{C}(C_2H_5)_2\\ \dot{C}OOC_2H_5\end{array}.$$

It is also possible to introduce two different alkyl-groups into diethyl malonate. Thus, when diethyl monosodiomalonate is treated with *methyl* iodide, the diethyl ester of methylmalonic acid is formed: on treatment with sodium this again yields a sodio-compound, which is converted by *ethyl* iodide into the diethyl ester of methylethylmalonic acid.

From these examples it is evident that it is possible to synthesize a great number of dibasic acids from diethyl malonate. Moreover, since all these acids contain two carboxyl-groups linked to the same carbon atom, and have in common with malonic acid the property of losing CO_2 when heated above their melting-points, it is evident that the so-called "malonic-ester synthesis" is also available for the preparation of the monobasic fatty acids. Thus, methylethylmalonic acid loses CO_2 on heating, yielding methylethylacetic acid, identical in constitution with active valeric acid (51), and resoluble into two active components:



$$\begin{array}{ccc} \mathrm{COOH} & & \mathrm{COOH} \\ \cdot & & \cdot \\ \mathrm{CH_3\cdot C\cdot C_2H_5} & = & \mathrm{CH_3\cdot C\cdot C_2H_5.} \\ \cdot & & \cdot \\ \boxed{\mathrm{COO}}\mathrm{H} & & \mathrm{H} \end{array}$$

Methylethylmalonic acid Valeric acid

The malonic-ester synthesis is much employed in the preparation of acids, and will be the subject of frequent reference.

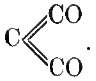
Details of the malonic-ester synthesis.—One gramme-molecule of diethyl malonate is mixed with a ten per cent. solution of sodium ethoxide (1 equivalent) in absolute alcohol, obtained by the action of sodium on alcohol. To this mixture is added one gramme-molecule of an alkyl iodide, and the reaction-mixture heated on a water-bath under a reflux-condenser until the liquid is no longer alkaline. After the alcohol has been distilled off, the residue is treated with water to dissolve the sodium iodide formed, and the diethyl alkylmalonate extracted with ether. The ethereal solution is dried over calcium chloride, the ether distilled, and the residue purified by fractionation.

If it is desired to introduce two alkyl-radicals or other groups, two equivalents of sodium ethoxide and two gramme-molecules of an alkyl iodide are employed. When two different groups are to be substituted, one of them is first introduced into the molecule, and on subsequent treatment with a second gramme-molecule of sodium ethoxide and of alkyl iodide, the diethyl dialkylmalonate is produced. Otherwise, the procedure is identical with that described above.

Carbon suboxide, C_3O_2, is formed by the distillation of dry malonic acid with ten times its weight of phosphoric oxide:

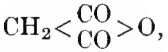
$$CH_2(COOH)_2 = C_3O_2 + 2H_2O.$$

This mode of formation indicates that carbon suboxide has the constitutional formula



$$C\begin{matrix}\diagup CO \\ \diagdown CO\end{matrix}.$$

It is a gas of very pungent odour, which can be condensed to a liquid boiling at 7°. With water, it regenerates malonic acid, and may, therefore, be regarded as an anhydride of this acid. The true anhydride,



$$CH_2<\begin{matrix}CO \\ CO\end{matrix}>O,$$

analogous to the anhydrides of the higher homologues of malonic acid, is unknown.

Succinic Acid, $COOH \cdot CH_2 \cdot CH_2 \cdot COOH$.

167. *Succinic acid* is a crystalline substance, melting at 182°, and dissolving with difficulty in cold water. It is present in amber, in fossilized wood, and in many plants, and can be synthetically prepared by the following methods.

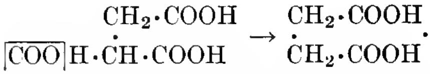
1. From ethylene bromide by treatment with potassium cyanide, which converts it into ethylene cyanide, $CN \cdot CH_2 \cdot CH_2 \cdot CN$: on hydrolysis, this yields succinic acid.

2. From malonic acid by treating diethyl monosodiomalonate with ethyl monochloroacetate:

$$(COOC_2H_5)_2CH\boxed{Na + Cl}H_2C \cdot COOC_2H_5 =$$
$$= NaCl + (COOC_2H_5)_2CH \cdot CH_2 \cdot COOC_2H_5.$$

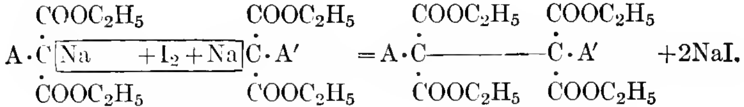
In this reaction an ester of *ethanetricarboxylic acid* is formed;

and when heated above its melting-point, the corresponding acid loses CO_2, yielding succinic acid:



$$\begin{array}{r} CH_2\cdot COOH\\ \cdot\\ \boxed{COO}H\cdot CH\cdot COOH \end{array} \rightarrow \begin{array}{l} CH_2\cdot COOH\\ \cdot\\ CH_2\cdot COOH \end{array}.$$

Succinic acid, and symmetrically substituted succinic acids, can also be obtained by the action of an ethereal solution of iodine or bromine upon diethyl monosodiomalonate or its monoalkyl-derivatives:

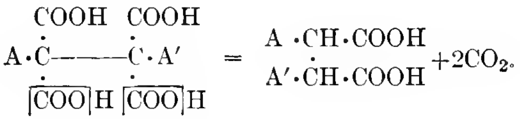


$$\begin{array}{lll} COOC_2H_5 & & COOC_2H_5\\ A\cdot C & \boxed{Na \quad +I_2+Na} & C\cdot A'\\ COOC_2H_5 & & COOC_2H_5 \end{array} = \begin{array}{ll} COOC_2H_5 & COOC_2H_5\\ A\cdot C\text{———} & \text{—}C\cdot A'\\ COOC_2H_5 & COOC_2H_5 \end{array} +2NaI.$$

A = Hydrogen or alkyl

Tetracarboxylic ester

By saponification, and elimination of CO_2, the ester formed is converted into the dibasic acid:



$$\begin{array}{ll} COOH & COOH\\ A\cdot C\text{———} & C\cdot A'\\ \boxed{COO}H & \boxed{COO}H \end{array} = \begin{array}{l} A\ \cdot CH\cdot COOH\\ \cdot\\ A'\cdot CH\cdot COOH \end{array} +2CO_2.$$

Electro-synthesis of Dibasic and Other Acids.

168. When the aqueous solution of an ester-salt of a dibasic acid is electrolyzed, the metallic ion goes to the cathode, the anion to the anode:

$$\overbrace{C_2H_5O\cdot OC\cdot CH_2\cdot COO}^{\text{Anion}}\quad \overbrace{K}^{\text{Cathion}}\ .$$

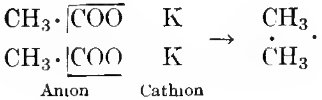
Ethyl potassium malonate

This anion, however, is not stable; after being discharged at the anode, it decomposes into carbon dioxide and $C_2H_5OOC\cdot CH_2$—, and two of these residues unite to form diethyl succinate:

$$C_2H_5OOC\cdot CH_2\text{—}CH_2\cdot COOC_2H_5.$$

By this method it is possible to synthesize the higher dibasic acids from the lower. A high *current-density* is necessary; that is, the number of ampères entering or leaving the electrode per square centimetre of surface. This is attained by employing a very small anode. The concentration of the anions discharged at the anode is proportional to the current-strength—the number of ampères—so that with a high current-density there is a great number of discharged anions at the anode, and these can interact readily.

This synthesis of dibasic acids is an extension of an electrosynthesis carried out long ago by Kolbe. He showed that on electrolysis a solution of potassium acetate yields ethane:



$$\begin{array}{lcl} CH_3\cdot\boxed{COO}\quad K & & CH_3 \\ CH_3\cdot\boxed{COO}\quad K & \rightarrow & \cdot \\ & & CH_3 \end{array}$$

Anion Cathion

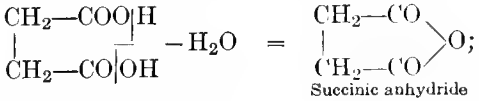
Many other extensions are known: thus, a mixture of a salt of a monobasic fatty acid and an ester-salt yields at the anode the ester of a monobasic acid:

$$\underset{\text{Potassium acetate}}{CH_3\cdot|COO\boxed{K}} + \underset{\text{Ethyl potassium succinate}}{\boxed{K}OOC\cdot|CH_2\cdot CH_2\cdot COOC_2H_5} \rightarrow$$

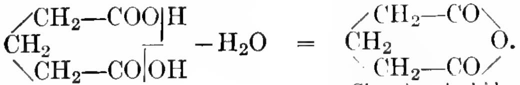
$$\rightarrow \underset{\text{Ethyl butyrate}}{CH_3\cdot CH_2\cdot CH_2\cdot COOC_2H_5}.$$

Formation of Anhydrides.

169. Oxalic acid and malonic acid do not yield anhydrides (**166**), while succinic acid, $C_4H_6O_4$, and glutaric acid, $C_5H_8O_4$, do so very readily. The formation of anhydride is due to the elimination of one molecule of water from one molecule of the dibasic acid, as is proved by a determination of the molecular weights of the anhydrides:

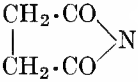


Succinic anhydride



Glutaric anhydride

These anhydrides are reconverted into the corresponding dibasic acids by dissolving them in water.

A derivative of succinic acid, *succinimide*,  $\left.\begin{array}{l}CH_2\cdot CO \\ | \\ CH_2\cdot CO\end{array}\right> NH$, has a ring of four carbon atoms and one nitrogen atom: it is formed

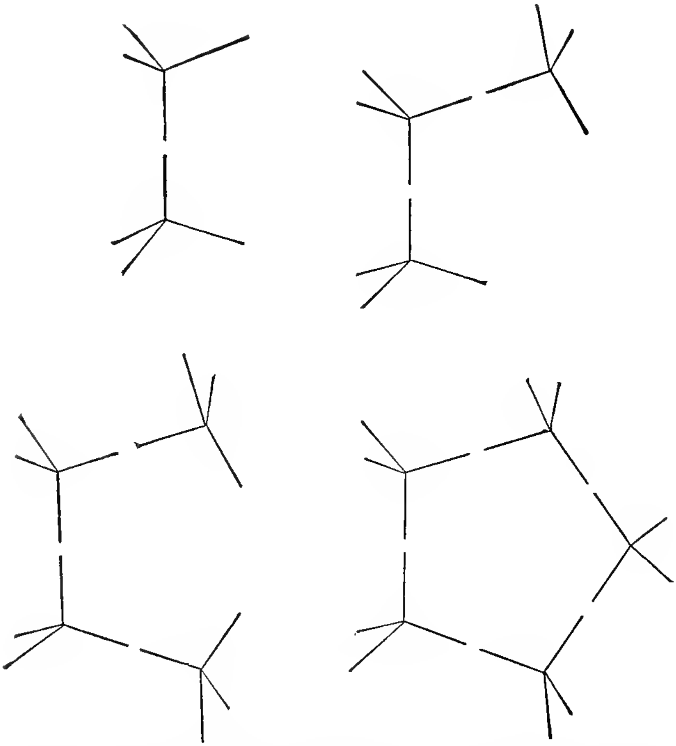
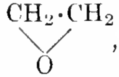


Fig. 33.—Spacial Representation of the Bonds between 2–5 C-atoms.

by the rapid distillation of ammonium succinate. The atoms situated at the extremities of a carbon chain of four or five C-atoms interact very readily: those in shorter chains only interact with difficulty, or not at all. Analogous phenomena are the elimination of one molecule of water from $\alpha\alpha'$-glycols (156), and of ammonia from $\alpha\alpha'$-diamines (162), both very readily effected from a carbon chain of four or five C-atoms, but impossible, or leading to the formation of very unstable compounds, when the chain is shorter. A satisfactory explanation of these phenomena, and others of the same type, may be attained by a consideration of the direction of the bonds in space. It was assumed (52) that the four affinities of the carbon atom are directed towards the angles of a regular tetrahedron with the carbon atom at the centre. For a single bond between two carbon atoms it is assumed that one affinity of each of these atoms is linked to one affinity of the other (Fig. 33). The position in space of the C-atoms in a chain of three or more members, and the direction of their affinities, are represented in the figure.

It is evident that in a normal chain of four C-atoms the affinities at the extremities approach one another closely, and in a chain of five C-atoms still more closely, so that they can interact readily.

A few instances of compounds with a closed chain containing only two C-atoms, such as ethylene oxide,  $\overset{CH_2\cdot CH_2}{\underset{O}{\diagdown\diagup}}$, are known. The figure indicates that for two C-atoms the direction of the affinities must undergo a considerable change to render the formation of a ring possible. Such compounds are unstable, the closed chain being very readily opened, as is indicated by the "strain-theory" of VON BAEYER (129).

II. UNSATURATED DIBASIC ACIDS.

Fumaric Acid and Maleïc Acid, $C_4H_4O_4$.

170. The most important members of the group of unsaturated dibasic acids are *fumaric acid* and *maleïc acid,* both with the formula $C_4H_4O_4$. They have been much investigated, a complete explanation of their isomerism having been finally arrived at by an application of the principles of stereoisomerism.

Fumaric acid is somewhat widely distributed in the vegetable kingdom. It does not melt at the ordinary pressure, but sublimes at about 200°: it dissolves with difficulty in water. Maleïc acid is not a natural product: it melts at 130°, and is very readily soluble in water.

Both acids can be obtained by heating malic acid (**190**),

$$\mathrm{COOH\cdot CHOH\cdot CH_2\cdot COOH,}$$

the result depending on the temperature and duration of the reaction. Fumaric acid is the principal product when the temperature is maintained at 140°–150° for a long time, but when a higher temperature is employed, and the heating is quickly carried out, the anhydride of maleïc acid distils along with water. This anhydride readily takes up water, regenerating the acid. This is the ordinary method for the preparation of these acids, and it indicates that both have the same structural formula:

$$\mathrm{COOH\cdot}\underset{\boxed{\mathrm{OH\ H}}}{\mathrm{\underset{\cdot}{CH}\cdot\underset{\cdot}{CH}}}\mathrm{\cdot COOH - H_2O = COOH\cdot CH:CH\cdot COOH.}$$

This view of their constitution is supported by the fact that on treatment with sodium-amalgam and water both acids yield succinic acid, and also by the formation of monobromosuccinic acid by addition of HBr, and of malic acid by heating with water at a high temperature. Both acids have therefore the same constitutional formula,

$$\mathrm{COOH\cdot CH:CH\cdot COOH.}$$

The isomerism of the crotonic acids is similar (**143**). It remains to consider how this isomerism can be explained by the aid of stereochemistry.

A single bond between two carbon atoms may be represented as in Fig. 34 (169). If the tetrahedra are drawn in full, then the single bond will be as in Fig. 35. If the tetrahedra are free to rotate round their common axis, isomerism cannot be expected for compounds $Cabc—Cdef$, nor has it ever been observed.

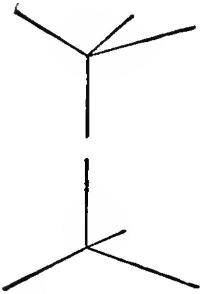


Fig. 34.

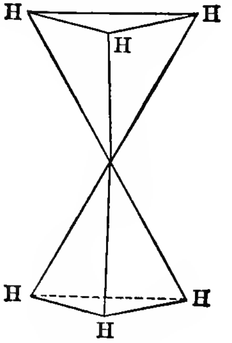


Fig. 35.

Single Bond between two Carbon Atoms.

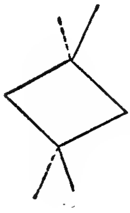


Fig. 36.

or

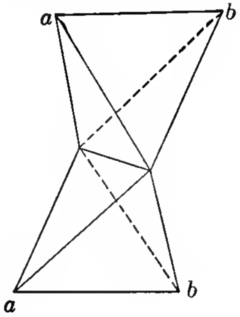


Fig. 37.

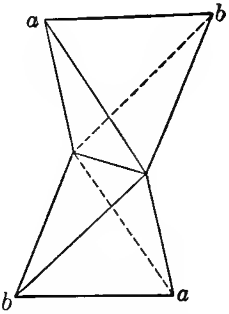
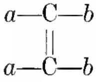


Fig. 38.

Graphic Spacial Representation of the Double Bond between two Carbon Atoms.

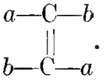
When a double bond is present, then two affinities of each carbon atom come into play, as graphically represented in Figs. 36, 37, and 38. Free rotation of the tetrahedra relative to one another is then no longer possible.

The figures indicate that difference of grouping depends on the position of the groups *a* and *b* of one tetrahedron with reference to the similar groups *a* and *b* of the other. *a* may be over *a*, and *b* over *b*, as in Fig. 37: or *a* may be over *b*, and *b* over *a*, as in Fig. 38. This can be represented by the formulæ



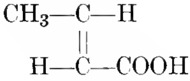
$$\begin{array}{c} a\text{—C—}b \\ \| \\ a\text{—C—}b \end{array}$$

and



$$\begin{array}{c} a\text{—C—}b \\ \| \\ b\text{—C—}a \end{array}.$$

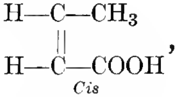
Thus, the two crotonic acids would be



$$\begin{array}{c} CH_3\text{—C—H} \\ \| \\ \text{H—C—COOH} \end{array}$$

Trans

and

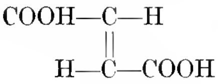


$$\begin{array}{c} \text{H—C—}CH_3 \\ \| \\ \text{H—C—COOH} \end{array},$$

Cis

and fumaric and maleïc acids would have the formulæ

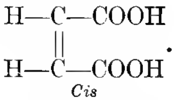
I.



$$\begin{array}{c} \text{COOH—C—H} \\ \| \\ \text{H—C—COOH} \end{array}$$

Trans

and II.

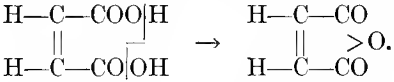


$$\begin{array}{c} \text{H—C—COOH} \\ \| \\ \text{H—C—COOH} \end{array}.$$

Cis

It must now be proved which of these two formulæ belongs to fumaric acid, and which to maleïc acid.

Maleïc acid yields an anhydride, while fumaric acid does not. In formula II. the carboxyl-groups are in juxtaposition to one another, but in formula I. they are as far removed from each other as possible. Only in the acid with the *cis*-formula are the carboxyl-groups represented in a position to interact readily:



$$\begin{array}{c} \text{H—C—COO|H} \\ \| \\ \text{H—C—CO|OH} \end{array} \rightarrow \begin{array}{c} \text{H—C—CO} \\ \| \quad >\text{O}. \\ \text{H—C—CO} \end{array}$$

Maleïc acid Maleïc anhydride

From this it is inferred that *fumaric acid has the constitution indicated in formula* I., *and maleïc acid that in formula* II.

171. Further consideration indicates that this view also accounts for the other known properties of these acids. Neither formula contains an asymmetric C-atom, so that neither optical activity nor the great resemblance in such properties as specific gravity, melting-point, solubility, etc., due to the similarity in internal structure characteristic of the isomerism occasioned by an asymmetric carbon atom, is to be expected. Fumaric acid and maleïc acid do, in fact, display great differences in these physical properties.

Both fumaric acid and maleïc acid combine with bromine, but the dibromo-addition-products thus obtained are different. Fumaric acid yields *dibromosuccinic acid*, soluble with difficulty in water; and maleïc acid iso*dibromosuccinic acid*, much more readily soluble in water. Figs. 39 to 42 indicate that different acids must result from this reaction. Figs. 40 and 42, representing dibromosuccinic acid and *iso*dibromosuccinic acid respectively, cannot be made to coincide by rotation; and this is made more evident by comparing Figs. 42 and 43. The latter is obtained from Fig. 40 by rotation of the upper tetrahedron round the vertical axis, the position of the lower tetrahedron remaining unaltered. In the figures the order of the groups linked to both carbon atoms of the *iso*-acid is H, Br, COOH from left to right: for the lower carbon atom of

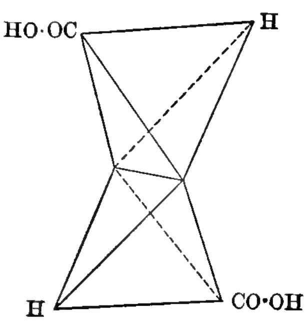


FIG. 39.—FUMARIC ACID.

$+ 2Br =$

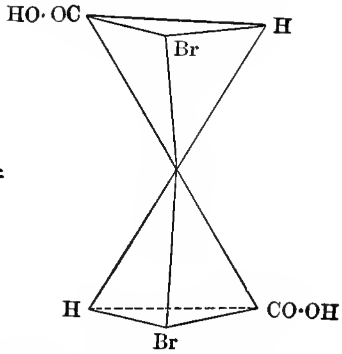


FIG. 40.—DIBROMOSUCCINIC ACID.

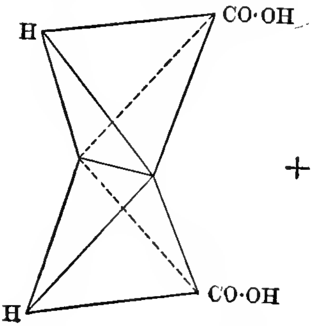


FIG. 41.—MALEÏC ACID.

$+ 2Br =$

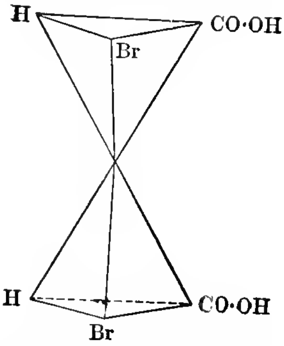


FIG. 42.—*iso*DIBROMOSUCCINIC ACID.

dibromosuccinic acid (Fig. 40) the order is similar, but for the upper carbon atom it is from right to left.

When HBr is removed from dibromosuccinic acid (Fig. 43), the H-atom linked to one carbon atom and the Br-atom linked to the other are eliminated, yielding an acid COOH·CH:CBr·COOH. This removal of HBr could not be effected if the tetrahedra were in the position shown in Fig. 40: rotation round the vertical axis is essential to bring H and Br into "corresponding" positions, as in Fig. 43: elimination of HBr produces the acid represented in Fig. 44. This acid readily yields an anhydride, since the COOH-groups are in the corresponding positions: it is therefore *bromo-maleïc acid.*

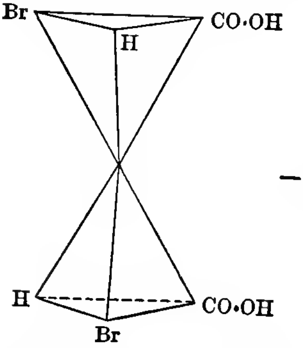


FIG. 43.—DIBROMOSUCCINIC ACID.

— HBr =

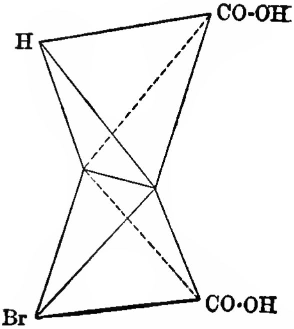


FIG. 44.—BROMOMALEÏC ACID.

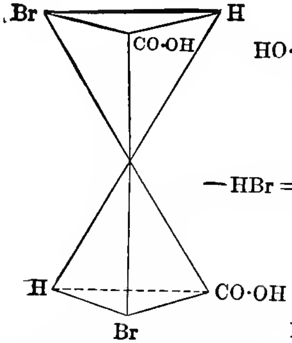


FIG. 45.—*iso*DIBROMOSUCCINIC ACID.

—HBr =

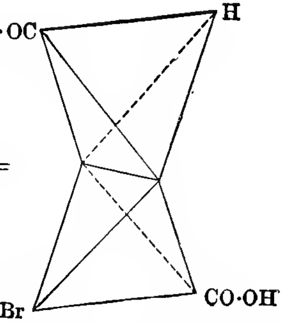


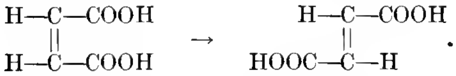
FIG. 46.—BROMOFUMARIC ACID.

When HBr is removed from *iso*dibromosuccinic acid, represented in Fig. 45 (obtainable from Fig. 42 by rotation in the same way as Fig. 43 from Fig. 40), an acid results which does not yield a corresponding anhydride, but is converted by elimination of water into the anhydride of bromomaleïc acid. This behaviour resembles that of fumaric acid, which under the same conditions yields maleïc anhydride. This acid must therefore be *bromofumaric acid* (Fig. 46).

It follows that the constitution assumed for these acids on stereochemical grounds accounts for their chemical properties. Another example which also supports this explanation is mentioned in 195.

Maleïc acid can be converted into fumaric acid by keeping it for some time at a temperature above its melting-point; by bringing it into contact with hydrogen halides at ordinary temperatures; by exposing its concentrated solution in presence of a trace of bromine to the action of sunlight, a slow reaction in absence of light; by treating ethyl maleate with small quantities of iodine; or by other means. The facility of all these decompositions indicates that maleïc acid is the unstable, and fumaric acid the stable, modification. Inversely, fumaric acid is converted by distillation into maleïc anhydride. The mechanism of these reactions is not fully understood.

The last reaction, as well as that by which maleïc acid is transformed into fumaric acid by the action of heat alone, can be explained by assuming an exchange of hydrogen and carboxyl at one of the doubly-linked C-atoms:



$$\begin{array}{c}\mathrm{H{-}C{-}COOH}\\ \|\\ \mathrm{H{-}C{-}COOH}\end{array} \rightarrow \begin{array}{c}\mathrm{H{-}C{-}COOH}\\ \|\\ \mathrm{HOOC{-}C{-}H}\end{array}.$$

Affinity-constants of the Unsaturated Acids.

172. Like the monobasic unsaturated acids (141), the dibasic unsaturated acids have greater affinity-constants than the corresponding saturated acids. For succinic acid, $10^4k=0\cdot665$, and for fumaric acid, $10^4k=9\cdot3$. The strength of acetylenedicarboxylic acid, $COOH\cdot C{\equiv}C\cdot COOH$ (obtained by the interaction of alcoholic potash and dibromosuccinic acid,

$$COOH\cdot CHBr{-}CHBr\cdot COOH),$$

is about equal to that of sulphuric acid. Thus, the presence of a double bond, and even more of a triple bond, intensifies the acidic character. For maleïc acid $10^4k = 117$, or about twelve times as much as for fumaric acid. This indicates the great influence exerted by the distance between the carboxyl-groups in the molecule upon the strength of these acids.

The ionization of dibasic acids is a step-by-step process. An acid H_2A first yields $\dot{H} + HA'$, and then on further dilution HA' is ionized to $\dot{H} + A''$. In this dissociation remarkable differences have been observed. For some acids the second stage of ionization does not begin until the first is almost complete, but for other acids it is already begun when about half of the first stage is over. The degree of ionization depends upon the relative position of the carboxyl-groups in the molecule. The nearer these groups are to each other, the more extended is the first, and the smaller the second, stage of ionization; and *vice-versa.*

This phenomenon is readily explained by assuming that the negative charge of the anion is concentrated on the hydroxyl-oxygen of the ionized carboxyl-group. During the ionization of the first H-atom, the presence of one carboxyl-group promotes the ionization of the other. This influence is greatest when the carboxyl-groups are close together. Other negative groups produce a similar effect (178 and 183). When, however, the ionization of the first H-atom is complete, the HA'-residue is decomposed with difficulty into H and A'', on account of the attraction exerted by the negative charge of this residue on any positively-charged H-ion liberated, this attraction being greatest when the negative charge is close to the H-atom of the HA'-residue. On the assumption that this charge is situated on the hydroxyl-oxygen of the first carboxyl-group, its attraction is greatest when the two carboxyl-groups in the non-ionized acid are in close proximity. When, however, the H-atom of the first carboxyl-group and the negatively-charged hydroxyl-oxygen of the HA'-residue are further apart, the second stage of the ionization meets with less resistance, and therefore takes place more readily.

173. VON BAEYER has prepared dibasic acids containing more than one triple bond in the molecule from acetylenedicarboxylic acid. When heated with water, its potassium hydrogen salt is converted into potassium propiolate (145), with loss of CO_2:

$$KOOC\cdot C{\equiv}C\cdot|\overline{CO_2}|H = CO_2 + KOOC\cdot C{\equiv}CH.$$

When the copper derivative of this salt, $KOOC{\cdot}C{\equiv}Ccu$,* is treated with potassium ferricyanide in alkaline solution, CuO is formed, while the two acid-residues simultaneously unite with production of the potassium salt of *diacetylenedicarboxylic acid,*

$$KOOC{\cdot}C{\equiv}C{-}C{\equiv}C{\cdot}COOK.$$

The potassium hydrogen salt of this acid also loses CO_2 readily, and the copper derivative of the monobasic acid thus formed is converted by similar oxidation into CuO and the potassium salt of *tetra-acetylenedicarboxylic acid:*

$$2KOOC{\cdot}C{\equiv}C{\cdot}C{\equiv}Ccu^* \rightarrow KOOC{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}COOK.$$

These compounds are very unstable, being decomposed by the action of light, and otherwise.

III. POLYBASIC ACIDS.

174. Acids with three carboxyl-groups in union with one carbon atom are unknown, except as esters. The triethyl ester of *methanetricarboxylic acid* is obtained by the action of ethyl chlorocarbonate (**269**) on diethyl monosodiomalonate:

$$C_2H_5OOC\boxed{Cl+Na}CH(COOC_2H_5)_2 = C_2H_5OOC{\cdot}CH(COOC_2H_5)_2.$$
Ethyl chlorocarbonate

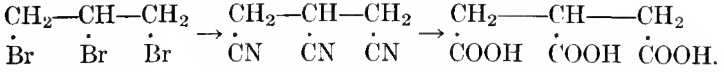
When this ester is saponified, CO_2 is simultaneously eliminated, malonic acid being formed instead of the corresponding tribasic acid. This is another instance of the phenomenon that *several negative groups do not remain in union with one carbon atom,* two being the maximum number for carboxyl (**155** and **180**).

A description of the syntheses of a few of the polybasic acids will afford examples of the methods adopted for the preparation of compounds of this class.

Tribasic Acids.

175. A type of the *tribasic acids* is *α,βα′-propanetricarboxylic acid,* or tricarballylic acid, obtainable by several methods.

1. From tribromohydrin by treatment with potassium cyanide, and hydrolysis of the tricyanohydrin thus formed:

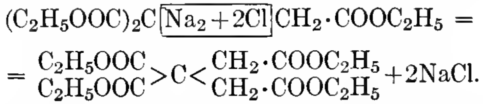


$$\underset{Br}{CH_2}{-}\underset{Br}{CH}{-}\underset{Br}{CH_2} \rightarrow \underset{CN}{CH_2}{-}\underset{CN}{CH}{-}\underset{CN}{CH_2} \rightarrow \underset{COOH}{CH_2}{-}\underset{COOH}{CH}{-}\underset{COOH}{CH_2}.$$

---

* $cu = \frac{1}{2}Cu$.

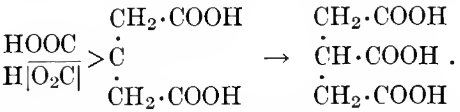
2. From diethyl disodiomalonate and ethyl monochloroacetate:



$$(C_2H_5OOC)_2C\boxed{Na_2+2Cl}CH_2\cdot COOC_2H_5 =$$

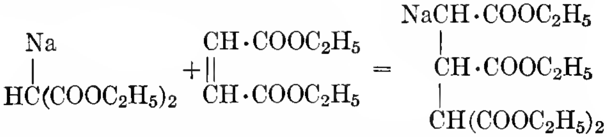
$$= \begin{matrix}C_2H_5OOC\\C_2H_5OOC\end{matrix}>C<\begin{matrix}CH_2\cdot COOC_2H_5\\CH_2\cdot COOC_2H_5\end{matrix}+2NaCl.$$

On saponification of this ester, an acid is obtained which on heating loses CO_2, with formation of tricarballylic acid:



$$\begin{matrix} & CH_2\cdot COOH \\ \begin{matrix}HOOC\\H\boxed{O_2C}\end{matrix}> & \dot{C} \\ & \dot{C}H_2\cdot COOH\end{matrix} \rightarrow \begin{matrix}CH_2\cdot COOH\\ \dot{C}H\cdot COOH\\ \dot{C}H_2\cdot COOH\end{matrix}.$$

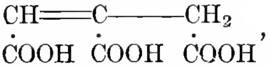
176. A synthesis peculiar to the polybasic acids consists in the *addition* of ethyl monosodiomalonate to the esters of unsaturated acids, such as fumaric acid:



$$\begin{matrix}Na\\|\\HC(COOC_2H_5)_2\end{matrix} + \begin{matrix}CH\cdot COOC_2H_5\\||\\CH\cdot COOC_2H_5\end{matrix} = \begin{matrix}NaCH\cdot COOC_2H_5\\|\\CH\cdot COOC_2H_5\\|\\CH(COOC_2H_5)_2\end{matrix}$$

Saponification, with subsequent elimination of CO_2, yields tricarballylic acid. It melts at 166°, and dissolves readily in water.

177. *Aconitic acid*, melts at 191°: it is a type of the *unsaturated tribasic acids*. It is obtained from citric acid (198) through removal of water by heating. The constitution of aconitic acid is



$$\begin{matrix}CH & = & C & - & CH_2\\ \dot{C}OOH & & \dot{C}OOH & & \dot{C}OOH\end{matrix},$$

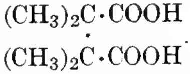
for on reduction it is converted into tricarballylic acid.

SUBSTITUTED ACIDS.

I. HALOGEN-SUBSTITUTED ACIDS.

178. The *halogen-substituted acids* can be obtained by the direct action of chlorine or bromine upon the saturated fatty acids, but this process is not very satisfactory. The monochloro-acids and monobromo-acids are best prepared by the action of chlorine or bromine, not upon the acid, but upon its chloride or bromide. The process involves treating the acid with phosphorus and a halogen, the phosphorus halide produced reacting with the acid to form an acid chloride or bromide, $R \cdot COX$, which is then attacked by the excess of halogen present.

Some acids cannot be thus brominated: such are trimethylacetic acid, $(CH_3)_3C \cdot COOH$, and tetramethylsuccinic acid,



$$\begin{array}{l}(CH_3)_2C \cdot COOH \\ \quad\quad\;\; \cdot \\ (CH_3)_2C \cdot COOH\end{array}$$

. In these acids there is no hydrogen in union with the α-carbon atom, which is directly linked to carboxyl. As a general rule, it is only possible to brominate acids of which the α-carbon atom is linked to hydrogen, the acids formed being called α-bromo-acids. The constitution of these is proved by converting them into hydroxy-acids (182), which are shown to be α-compounds through their synthesis by another method.

Halogen-substituted acids can also be prepared by addition of hydrogen halide or halogen to the unsaturated acids, or by the action of phosphorus halides on the hydroxy-acids. The iodo-acids can sometimes be advantageously obtained from the corresponding chloro-derivatives by heating them with potassium iodide.

The introduction of halogen into the molecule causes a marked increase in the strength of an acid, as will be seen from the table on next page of dissociation-constants, 10^4k.

Name.	Formula.	10^4k.
Acetic acid	$CH_3\cdot CO_2H$	0·18
Monochloroacetic acid	$CH_2Cl\cdot CO_2H$	15·5
Monobromoacetic acid	$CH_2Br\cdot CO_2H$	13·8
Monoiodoacetic acid	$CH_2I\cdot CO_2H$	7·5
Dichloroacetic acid	$CHCl_2\cdot CO_2H$	514
Trichloroacetic acid	$CCl_3\cdot CO_2H$	12100
Propionic acid	$CH_3\cdot CH_2\cdot CO_2H$	0·134
β-Iodopropionic acid	$CH_2I\cdot CH_2\cdot CO_2H$	0·90

This table indicates that the strength of an acid is increased to a greater extent by chlorine than by bromine, and by bromine than by iodine, and that a marked increase is occasioned by the introduction of more than one chlorine atom. The position of the halogen atom also exerts an influence: for iodoacetic acid with the I-atom in the α-position the value of the constant is 32 times as great as for acetic acid, while for β-iodopropionic acid 10^4k is only 7 times as great as for propionic acid.

179. The influence of the carboxyl-groups upon the halogen atoms is such that *the properties of the monohalogen-substituted acids depend chiefly upon the relative position of the halogen atom and the carboxyl-group.*

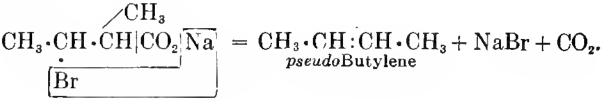
On boiling with alkalis, the α-halogen-substituted acids are readily converted into the α-hydroxy-acids by exchange of halogen for hydroxyl:

$$\underset{\text{Monochloroacetic acid}}{CH_2Cl\cdot COOH} + KOH = KCl + \underset{\text{Potassium glycollate}}{CH_2OH\cdot COOK}.$$

On similar treatment, the β-halogen-substituted acids lose hydrogen halide, with formation of unsaturated acids:

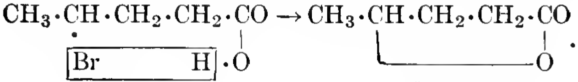
$$\underset{\beta\text{-Chlorobutyric acid}}{CH_3\cdot CHCl\cdot CH_2\cdot COOH} = \underset{\text{Crotonic acid}}{CH_3\cdot CH{:}CH\cdot COOH} + HCl.$$

The behaviour of the β-halogen-substituted acids with sodium carbonate is very characteristic. When they are warmed with its aqueous solution, hydrogen halide and CO_2 are simultaneously eliminated from the molecule, with formation of an unsaturated hydrocarbon:



$$CH_3\cdot\underset{\boxed{Br}}{CH}\cdot\overset{\diagup CH_3}{CH}\boxed{CO_2Na} = \underset{pseudo\text{Butylene}}{CH_3\cdot CH{:}CH\cdot CH_3} + NaBr + CO_2.$$

On boiling with water or with an alkali-metal carbonate, the γ-halogen-substituted acids readily lose HX, forming *lactones* (**183** and **187**):



$$\begin{array}{l} CH_3\cdot CH\cdot CH_2\cdot CH_2\cdot CO \\ \quad \boxed{Br \qquad\qquad H}\cdot O \end{array} \rightarrow \begin{array}{l} CH_3\cdot CH\cdot CH_2\cdot CH_2\cdot CO \\ \qquad \llcorner\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!- O \end{array}.$$

Valerolactone

Chloroacetic Acids.

180. *Monochloroacetic acid,* $CH_2Cl\cdot COOH$, is obtained by the action of chlorine upon acetic acid, in presence of sulphur as a chlorine-carrier. It is a crystalline solid, melting at 63°. *Dichloroacetic acid,* $CHCl_2\cdot COOH$, and *trichloroacetic acid,* $CCl_3\cdot COOH$, are best prepared from chloral (**201**). Trichloroacetic acid is unstable, and on boiling with water decomposes into carbon dioxide and chloroform:

$$CCl_3\cdot\boxed{CO_2}H = CCl_3H + CO_2.$$

This is another example of the fact that "loading" a carbon atom with negative elements and groups renders the molecule unstable.

Acids with more than one Halogen Atom in the Molecule.

181. Isomerism in this type of compounds may be occasioned by a difference in position of the halogen atoms in the molecule. Addition of halogen to an unsaturated acid produces a compound with the halogen atoms linked to adjoining carbon atoms.

The elimination of hydrogen halide from acids of this class affords a striking example of the value of stereochemistry in explaining phenomena for which the ordinary constitutional formulæ are unable to account. Among them is the fact that in the series of unsaturated acids the dibromide of one modification loses 2HBr very readily, yielding an acid with a triple bond, while the dibromide of the other modification either does not react thus, or only with difficulty. An example of this is afforded by erucic and brassidic acids, which have been proved, by the method indicated in **145**, to have the constitution

$$C_6H_{17}\cdot CH{:}CH\cdot C_{11}H_{22}\cdot COOH.$$

On addition of bromine, and subsequent heating with alcoholic potash at 150°–170°, dibromoerucic acid easily loses 2HBr, yielding *behenolic acid*, $C_8H_{17} \cdot C \equiv C \cdot C_{11}H_{22} \cdot COOH$; whereas one molecule of hydrobromic acid is eliminated from dibromobrassidic acid, with production of a monobromoerucic acid. This difference is accounted for by assigning the *trans*-formula to erucic acid and the *cis*-formula to brassidic acid, as indicated in Figs. 47 to 52.

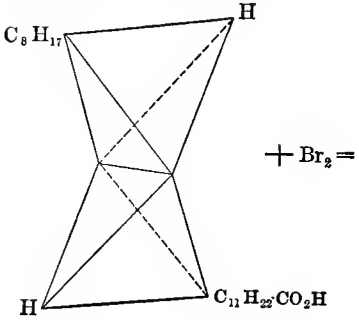


FIG. 47.—ERUCIC ACID.
Trans-formula.

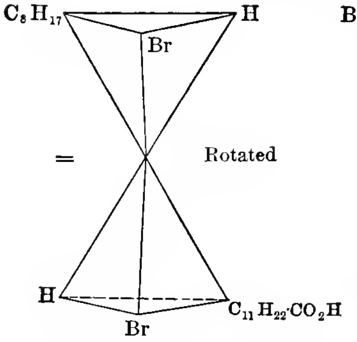


FIG. 48.—DIBROMOERUCIC ACID.

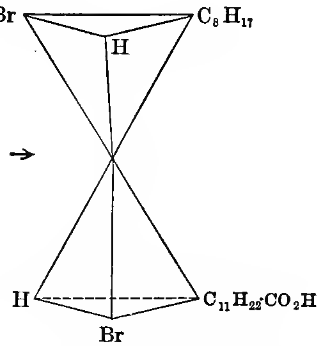


FIG. 49.—DIBROMOERUCIC ACID.
Each H-atom in corresponding position to a Br-atom.

In the formula for dibromoerucic acid, the tetrahedra may be rotated so as to bring each Br-atom above a H-atom (171), making the elimination of 2HBr possible (Figs. 48 and 49): in that for dibromobrassidic acid, only one Br-atom and one H-atom can be brought into the "corresponding positions" to one another (Figs. 51 and 52).

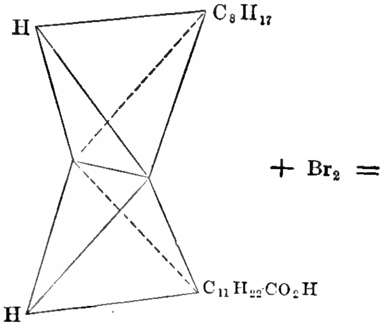


FIG. 50.—BRASSIDIC ACID.
Cis-formula.

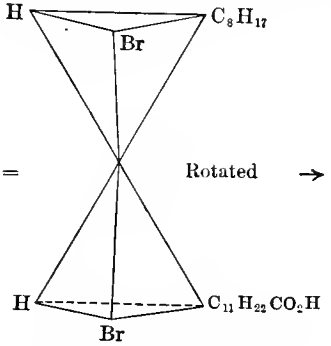


FIG. 51.—DIBROMOBRASSIDIC ACID.

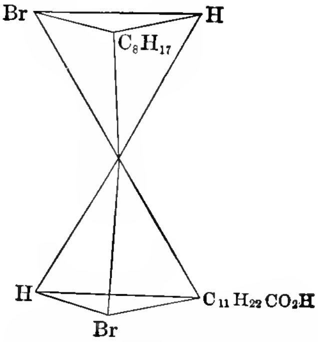


FIG. 52.—DIBROMOBRASSIDIC ACID.
Only one H-atom in corresponding position to one Br-atom.

II. MONOBASIC HYDROXY-ACIDS.

182. The *hydroxy-acids* are substances with one or more hydroxyl-groups and carboxyl-groups in the molecule. The general methods for their formation depend upon the introduction of hydroxyl-groups and carboxyl-groups. They are produced in the following reactions.

1. By the careful oxidation of polyhydric alcohols:

$$\underset{\text{Propyleneglycol}}{CH_3\cdot CHOH\cdot CH_2OH} \rightarrow \underset{\text{Lactic acid}}{CH_3\cdot CHOH\cdot COOH}.$$

2. By replacement of the halogen in halogen-substituted acids by hydroxyl, as already described (156).

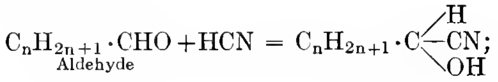
3. By reduction of the aldehydic acids and ketonic acids, which contain both a carboxyl-group and a carbonyl-group:

$$\underset{\text{Pyroracemic acid}}{CH_3{\cdot}CO{\cdot}COOH} + 2H = \underset{\text{Lactic acid}}{CH_3{\cdot}CHOH{\cdot}COOH}.$$

4. By the action of nitrous acid upon acids with an amino-group in the alkyl-residue:

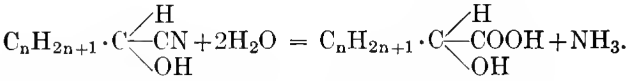
$$\underset{\text{Glycine}}{NH_2{\cdot}CH_2{\cdot}COOH} + HNO_2 = \underset{\text{Glycollic acid}}{CH_2OH{\cdot}COOH} + N_2 + H_2O.$$

5. By addition of hydrocyanic acid to aldehydes or ketones, and hydrolysis of the nitrile thus obtained (110, 3), a method yielding only α-hydroxy-acids:



$$\underset{\text{Aldehyde}}{C_nH_{2n+1}{\cdot}CHO} + HCN = C_nH_{2n+1}{\cdot}C\begin{cases}H\\CN;\\OH\end{cases}$$

Cyanohydrin

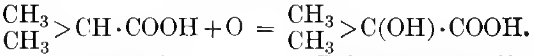


$$C_nH_{2n+1}{\cdot}C\begin{cases}H\\CN\\OH\end{cases} + 2H_2O = C_nH_{2n+1}{\cdot}C\begin{cases}H\\COOH\\OH\end{cases} + NH_3.$$

Cyanohydrin α-Hydroxy-acid

By exchange of Br for OH, acids brominated by the method described in 178 yield hydroxy-acids identical with those obtained by this *cyanohydrin-synthesis*. It follows that in these acids the bromine is in union with the α-carbon atom.

6. Oxidation with potassium permanganate effects the direct replacement of hydrogen by hydroxyl in acids with a hydrogen atom linked to a tertiary carbon atom:



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{\cdot}COOH + O = \begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH){\cdot}COOH.$$

*iso*Butyric acid α-Hydroxy*iso*butyric acid

Properties.

183. Different compounds are obtained from the hydroxy-acids by substitution in the hydroxyl-group and carboxyl-group respectively. When the H-atom of the hydroxyl-group is replaced by alkyl, an *acid ether* is obtained:

$$\underset{\text{Glycollic acid}}{CH_2OH{\cdot}COOH} \rightarrow \underset{\text{Ethylglycollic acid}}{CH_2OC_2H_5{\cdot}COOH}.$$

Like an ordinary ether, $C_nH_{2n+1}\cdot O\cdot C_mH_{2m+1}$, ethylglycollic acid cannot be saponified. When, on the other hand, the H-atom of the carboxyl-group is exchanged for alkyl, an ester is produced:

$$CH_2OH\cdot COOH \rightarrow CH_2OH\cdot COOC_2H_5.$$

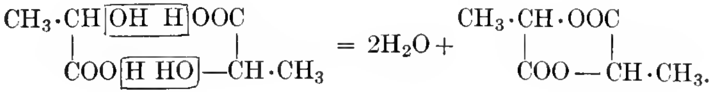
Ethyl glycollate

Like other esters, these compounds can be saponified.

The introduction of hydroxyl strengthens the fatty acids to an extent dependent on its position relative to the carboxyl-group, an effect analogous to that produced by the halogens (178). This is indicated by the table, which contains the values of the dissociation-constant, 10^4k, for several acids.

Name.	Formula.	10^4k.
Acetic acid.	$CH_3\cdot COOH$	0·180
Glycollic acid (Hydroxyacetic acid).	$CH_2OH\cdot COOH$	1·52
Propionic acid.	$CH_3\cdot CH_2\cdot COOH$	0·134
Lactic acid (α-Hydroxypropionic acid).	$CH_3\cdot CHOH\cdot COOH$	1·38
β-Hydroxypropionic acid.	$CH_2OH\cdot CH_2\cdot COOH$	0·311

On heating, the *α-hydroxy-acids* readily lose water, two molecules being simultaneously eliminated from two molecules of acid: this reaction takes place between the hydroxyl-group of one molecule and the carboxyl-group of the other. Lactic acid yields *lactide:*

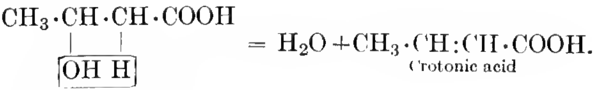


$$\begin{array}{l} CH_3\cdot CH\boxed{OH\quad H}OOC \\ \qquad | \qquad\qquad\qquad | \\ \quad COO\boxed{H\ HO}—CH\cdot CH_3 \end{array} = 2H_2O + \begin{array}{l} CH_3\cdot CH\cdot OOC \\ \qquad | \qquad\quad | \\ \quad COO — CH\cdot CH_3. \end{array}$$

Lactide

The formula of this compound indicates that it is a double ester, its constitution being proved by its behaviour when boiled with water or dilute acids: like the esters, it is saponified, yielding lactic acid.

β-Hydroxy-acids readily give up water, with formation of unsaturated acids:



$$\begin{array}{l} CH_3\cdot CH\cdot CH\cdot COOH \\ \qquad | \quad\ \ | \\ \quad \boxed{OH\ H} \end{array} = H_2O + CH_3\cdot CH{:}CH\cdot COOH.$$

β-Hydroxybutyric acid

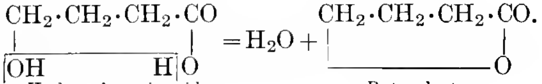
Crotonic acid

When a β-hydroxy-acid is boiled with excess of a 10 per cent. solution of caustic soda, it is partly converted into an αβ-unsaturated acid, and partly into a βγ-unsaturated acid, while a portion remains unchanged. An equilibrium is thus reached:

$$\text{R}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOH} \rightleftarrows \text{R}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{COOH} \rightleftarrows$$
$$\rightleftarrows \text{R}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{COOH}.$$

If this reaction is reversible, the same equilibrium should be attained by starting from the hydroxy-acid, or from either of the two unsaturated acids. Fittig proved that this is actually the case.

γ-Hydroxy-acids and *δ-hydroxy-acids* lose water, with formation of inner anhydrides, called *lactones* (179 and 187):



$$\begin{array}{l}\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\\ |\qquad\qquad\qquad\qquad |\\ \boxed{\text{OH}\qquad\qquad \text{H}}\text{O}\end{array} = \text{H}_2\text{O} + \begin{array}{l}\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}.\\ |\qquad\qquad\qquad\qquad |\\ \underline{\qquad\qquad\qquad\qquad}\text{O}\end{array}$$

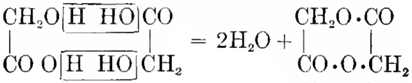
γ-Hydroxybutyric acid Butyrolactone

Glycollic Acid, $C_2H_4O_3$.

184. *Glycollic acid* is present in unripe grapes. It is usually prepared by treating monochloroacetic acid with caustic potash:

$$\text{COOH}\cdot\text{CH}_2\boxed{\text{Cl} + \text{K}}\text{OH} = \text{COOH}\cdot\text{CH}_2\text{OH} + \text{KCl}.$$

Glycollic acid is a crystalline solid, melting at 80°. It is very readily soluble in water, alcohol, and ether: the calcium salt dissolves with difficulty in water. When distilled *in vacuo*, glycollic acid loses water, with formation of glycollide:



$$\begin{array}{l}\text{CH}_2\text{O}\boxed{\text{H}\ \ \text{HO}}\text{CO}\\ |\qquad\qquad\qquad |\\ \text{CO O}\boxed{\text{H}\ \ \text{HO}}\text{CH}_2\end{array} = 2\text{H}_2\text{O} + \begin{array}{l}\text{CH}_2\text{O}\cdot\text{CO}\\ |\qquad\qquad |\\ \text{CO}\cdot\text{O}\cdot\text{CH}_2\end{array}$$

Glycollide

Hydroxypropionic Acids, $C_3H_6O_3$.

185. Two *hydroxypropionic acids* are known, differing in the position occupied by the hydroxyl-group: they are *α-hydroxypropionic acid*, $CH_3\cdot CHOH\cdot COOH$, and *β-hydroxypropionic acid*, $CH_2OH\cdot CH_2\cdot COOH$. The first is ordinary *lactic acid*.

α-Hydroxypropionic acid can be obtained synthetically by the methods described in 182, although it is usually prepared by other means. In presence of an organized ferment, called the "lactic-acid bacillus," certain sugars, such as lactose, sucrose, and dextrose, undergo "lactic fermentation," the principal product being lactic acid. These bacilli are present, for example, in decaying cheese, and cannot live in a solution of lactic acid of more than a certain concentration: to make fermentation possible, chalk is added to neutralize the lactic acid formed. Lactic acid can also be prepared by heating dextrose or invert-sugar with caustic soda.

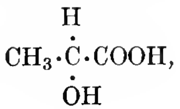
Lactic acid derives its name from its presence in sour milk, as a result of the fermentation of the lactose present. The faint acid odour possessed by sour milk is due, not to lactic acid, but to traces of volatile fatty acids simultaneously formed: lactic acid itself is odourless. Lactic acid is also present in other fermented substances, such as "Sauerkraut"; and in large quantities in ensilage, a cattle-food prepared by submitting piles of grass or clover to pressure.

Lactic acid is purified by distilling the aqueous acid at very low pressures (1 mm.), when it is obtained as a crystalline solid melting at 18°. The commercial product is a colourless, syrupy liquid of strongly acid taste, and contains water. When heated under ordinary pressure, with the object of removing water, it is partially converted into the anhydride (183) even before dehydration is complete: this can be detected by the diminution of the acid-equivalent on titration. Its zinc salt forms well-defined crystals with three molecules of water.

The constitution of lactic acid is deduced from its formation from acetaldehyde by the cyanohydrin-synthesis (182, 5), and by the oxidation of propyleneglycol. When lactic acid is heated alone, or with dilute sulphuric acid, it yields acetaldehyde and formic acid:

$$CH_3{\cdot}CHO\boxed{H{\cdot}COOH} \rightarrow CH_3{\cdot}C^{H}_{O}+H{\cdot}COOH.$$

This decomposition may be regarded as a reversal of the cyanohydrin-synthesis, and is characteristic of many α-hydroxy-acids.



Lactic acid, $CH_3{\cdot}\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}{\cdot}COOH$, contains one asymmetric carbon atom. In accordance with the principles laid down in **53**, it ought to exist in three isomeric modifications, and all these are known. Ordinary lactic acid obtained by synthesis is *racemic:* that is, it consists of equal quantities of the dextro-acid and lævo-acid, and is therefore optically inactive. Dextro-lactic acid and lævo-lactic acid can be obtained from the inactive modification by methods described in **196**. The dextro-rotatory variety is a constituent of meat-juices, and is therefore sometimes called "sarcolactic acid."

186. The synthetic lactic acid is inactive, and hitherto optically active products have not been prepared from inactive substances by wholly chemical means. Since the inactive modification consists of equal parts of dextro-rotatory and lævo-rotatory substance, both must be formed in equal quantities in the synthesis. An explanation of this phenomenon is afforded by a consideration of the following examples.

The nitrile of lactic acid is obtained by the addition of hydrocyanic acid to acetaldehyde (**182**, 5), the structural formula of which is represented in Fig. 53:

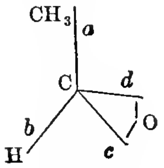


FIG. 53.
ACETALDEHYDE.

→

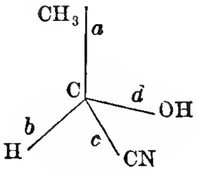


FIG. 54.
LACTONITRILE.

or

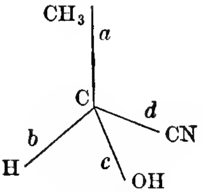


FIG. 55.
LACTONITRILE.

The addition of H·CN can take place in two ways, the oxygen doubly linked to the central carbon atom of the figure becoming severed either from the bond *c* or from *d*. In the first case the group CN becomes linked to *c* (Fig. 54), and a hydroxyl-group is formed at *d*: in the second case this is reversed (Fig. 55). The configurations thus obtained are mirror-images, and cannot be made to coincide: they represent asymmetric C-atoms.

The possibility of the formation of both active components is thus evident, and that these must be formed in equal amounts is made clear by a consideration of the *probability* of their formation. This is alike for both, since *d* and *c* occupy similar positions with respect to *a* and *b*, and there is therefore no tendency for the oxygen to remain linked to the one more than to the other.

In this example an asymmetric carbon atom has resulted from an *addition*-reaction. An example of the formation by *substitution* of a compound containing such an atom is that of α-bromopropionic acid, $\begin{matrix}\mathrm{Br}\\\mathrm{H}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_3}\\\mathrm{COOH}\end{matrix}$, from propionic acid, $\begin{matrix}c\mathrm{H}\\d\mathrm{H}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_3}\\\mathrm{COOH}\end{matrix}$. By replacement of H*c* and H*d* respectively, two acids of opposite rotation are produced, the probability of the formation of one being equal to that of the formation of the other.

Compounds containing an asymmetric carbon atom can also result from the elimination of a group, as in the formation of methylethylacetic acid, $\begin{matrix}\mathrm{CH_3}\\\mathrm{C_2H_5}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{H}\\\mathrm{COOH}\end{matrix}$, from methylethylmalonic acid, $\begin{matrix}\mathrm{CH_3}\\\mathrm{C_2H_5}\end{matrix}>\mathrm{C}<\begin{matrix}c\\\mathrm{COOH}\\\mathrm{COOH}\\d\end{matrix}$, by loss of CO_2. The probability that this will take place at *c* and at *d* is equal, so that an inactive mixture is produced.

When optically active lactic acids and other optically active substances are strongly heated, they are converted into the corresponding optically inactive form, containing equal proportions of the dextro-modification and lævo-modification. This necessitates the conversion of one-half of the optically active substance into its optical isomeride, it being sufficient that two of the groups or atoms linked to the asymmetric C-atom should change places. To convert Fig. 56 into its mirror-image, Fig. 57, it is only necessary, for example, for B and D to exchange positions. This can only happen through a severance of the bonds between B and D and the carbon atom, for a period however brief, followed by a reunion, either as

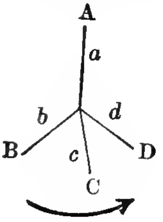


FIG. 56.

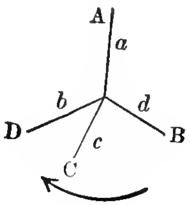


FIG. 57.

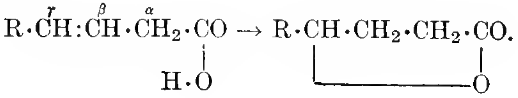
at first B to *b* and D to *d*, or in the reverse order D to *b* and B to *d*. The similarity of the positions occupied by *b* and *d* with respect to *a* and *c* makes the probability of the union of B with *b* and D with *d* equal to that of the union of D with *b* and B with *d*, so that dextro-rotatory and lævo-rotatory molecules are formed in equal numbers, and after heating the substance is optically inactive.

Optical inactivity is sometimes attained without the aid of heat. Waloen found that the dextro-rotatory *iso*butyl bromopropionate, $CH_3{\cdot}CHBr{\cdot}COOC_4H_9$, and other compounds with a Br-atom in union with an asymmetric C-atom, became optically inactive through being kept for three or four years at the ordinary temperature. The velocity of transformation under such conditions, for most substances too small to be appreciable after the lapse of even long periods—and only measurable at higher temperatures, which have an accelerating effect upon most reactions—has for these compounds a measurable value.

Lactones.

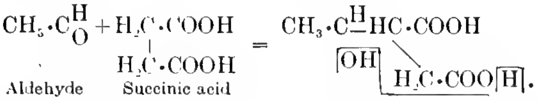
187. The γ-hydroxy-acids lose water very readily, with formation of *lactones* (179 and 183). So great is this tendency that some γ-hydroxy-acids, when liberated from their salts, at once give up one molecule of water, yielding a lactone. This phenomenon is another example of the readiness with which ring-compounds containing four carbon atoms are formed (169). Many γ-hydroxy-acids are not known in the free state, but only in the form of esters, salts, or amides. The lactones are stable towards an aqueous solution of sodium carbonate, but are converted by the hydroxides of the alkali-metals into salts of γ-hydroxy-acids, a reaction proving their constitution. They may be looked upon as the inner esters of the hydroxy-acids.

The lactones can be prepared by several methods. Thus, acids containing a double bond at the $\beta\gamma$-position or $\gamma\delta$-position ($\Delta^{\beta\gamma}$-acids or $\Delta^{\gamma\delta}$-acids) are readily converted into lactones by warming with dilute sulphuric acid. This formation of lactones may be regarded as an addition of the carboxyl-group at the double bond:

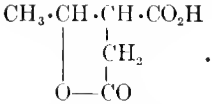


$$\mathrm{R{\cdot}\overset{\gamma}{C}H{:}\overset{\beta}{C}H{\cdot}\overset{\alpha}{C}H_2{\cdot}\underset{\underset{H\cdot O}{|}}{CO}} \rightarrow \mathrm{R{\cdot}\underbrace{CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO}_{O}.}$$

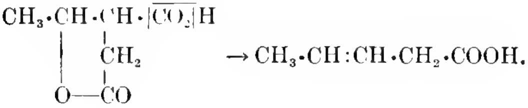
Unsaturated $\Delta^{\beta\gamma}$-acids can be obtained by several methods, one being the action of aldehydes upon sodium succinate in presence of acetic anhydride:



By elimination of one molecule of water, there results a lactonic acid,

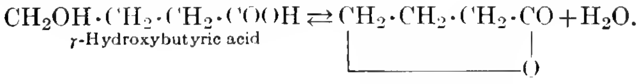


On dry distillation, this loses CO_2, yielding the unsaturated acid:



Another method for the preparation of lactones is the reduction of γ-ketonic acids (251, 3). δ-Lactones and ε-lactones are also known.

On boiling with water, the lactones are partly converted into the corresponding hydroxy-acids, the quantity of acid formed being in a measure dependent upon the amount of water present. An equilibrium is attained between the system acid and lactone + water:



188. If the molecular concentration per litre of the γ-hydroxy-butyric acid is A, and if, after the lapse of a time t, x molecules have been converted into lactone, the velocity of lactone-formation at that instant, s, is given by the equation

$$s=k(A-x),$$

k being the reaction-constant. But the reverse also takes place, the acid being regenerated from the lactone and water. If the lactone is dissolved in a large excess of water, no appreciable error is introduced by assuming the quantity of the latter to be constant. The velocity s' of this reverse reaction is then represented by the equation

$$s' = k'x,$$

in which k' is again the reaction-constant. The total velocity of the lactone-formation for each instant is, therefore, equal to the difference between these velocities:

$$s - s' = \frac{dx}{dt} = k(A - x) - k'x. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When equilibrium is reached, $s = s'$; and if the value of x at this point has become equal to x_1, then

$$k(A - x_1) - k'x_1 = 0, \quad \text{or} \quad \frac{k}{k'} = \frac{x_1}{A - x_1}. \quad . \quad . \quad . \quad (2)$$

Equations 1 and 2 can be solved for k and k'. The same method of calculation may be applied to ester-formation from acid and alcohol, by which the reaction-constant of the ester-formation, and of the ester-decomposition, can be computed.

The lactones form addition-products with hydrobromic acid as well as with water, yielding γ-bromo-acids, the constitution of which is inferred from their reconversion into lactone (**179**). The lactones also form addition-products with ammonia, yielding the amides of the γ-hydroxy-acids.

III. DIBASIC HYDROXY-ACIDS.

189. The simplest *dibasic hydroxy-acid* is *tartronic acid*, COOH·CHOH·COOH. It can be obtained by the action of moist oxide of silver upon bromomalonic acid, and is a crystalline solid, melting at 187° with evolution of CO_2. The glycollic acid, $CH_2OH \cdot COOH$, thus formed, at once loses water, yielding a polymeride of glycollide (**184**).

190. A substance of greater importance is *malic acid*, $C_4H_6O_5$, which is present in various unripe fruits, and is best prepared from unripe mountain-ash berries. It is a crystalline solid, melting at

100°, and is readily soluble in water and in alcohol. Natural malic acid is optically active.

It is possible to prove in several ways that malic acid is hydroxysuccinic acid, $COOH \cdot CHOH \cdot CH_2 \cdot COOH$. Among these are its reduction to succinic acid by heating with hydriodic acid, its conversion into monochlorosuccinic acid by the action of phosphorus pentachloride, and so on. Its alcoholic character is indicated by the formation of an acetate when its diethyl ester is treated with acetyl chloride.

The conversion of malic acid under the influence of heat into fumaric acid and maleïc acid has been already mentioned (**170**). In addition to the natural lævo-rotatory acid, both a dextro-rotatory and an inactive modification are known. The latter can be resolved by fractional crystallization of its cinchonine salt into its two optically active components. As indicated by its structural formula, malic acid contains an asymmetric C-atom.

Tartaric Acids, $C_4H_6O_6$.

191. Four acids of the composition $C_4H_6O_6$ are known, all with the constitutional formula

$$COOH \cdot CHOH \cdot CHOH \cdot COOH.$$

They are called *dextro-rotatory tartaric acid, lævo-rotatory tartaric acid, racemic acid*, and *mesotartaric acid:* the last two are optically inactive. Their constitution is proved by their formation from the dibromosuccinic acids—obtained from fumaric acid or maleïc acid by the action of bromine—by boiling their silver salts with water, as well as by their production from glyoxal (**199**) by the cyanohydrin synthesis. The inactive modifications are produced by these reactions (**186**).

In accordance with the constitutional formula given above, the tartaric acids contain two asymmetric C-atoms in the molecule, and it is necessary to consider how many stereoisomerides are theoretically possible.

The formula of such a substance can be represented by $C(abc)—C(def)$. The groups linked to the asymmetric C-atoms are in this general formula dissimilar: the two asymmetric C-atoms are assumed to be unlike. Since the mode of arrangement of the groups relative to each of these C-atoms results in dextro-rotation and lævo-rotation respectively, the combinations possible in the molecule of a substance containing two asymmetric C-atoms are:

	1	2	3	4
C(*abc*)	Dextro	Dextro	Lævo	Lævo
C(*def*)	Dextro	Lævo	Lævo	Dextro

There are, therefore, four isomerides possible, apart from the optically inactive modifications containing equal quantities of two of these (1 and 3, 2 and 4).

Since tartaric acid, however, contains two *similar* asymmetric C-atoms, that is asymmetric C-atoms in union with similar groups, 2 and 4 become identical, leaving so far three isomerides possible. 1 and 3 being able to unite to form a racemic compound, the total number of possible isomerides is raised to four:

	1	2	3	4
CH(OH)(COOH)	Dextro	Dextro	Lævo	Inactive combination of 1 and 3
CH(OH)(COOH)	Dextro	Lævo	Lævo	

The four tartaric acids, $C_4H_6O_6$, correspond in properties with the four theoretically possible isomerides. Dextro-tartaric acid and lævo-tartaric acid must be represented respectively by 1 and 3, since in these both C-atoms rotate the plane of polarization in the same direction, and should therefore reinforce each other's influence. The optically inactive mesotartaric acid is represented by 2: its two asymmetric C-atoms rotate the plane of polarization equally, but in opposite directions, and thus neutralize each other's effect. Finally, isomeride 4 is racemic acid.

An important difference exists between the two optically inactive isomerides, racemic acid and mesotartaric acid. The former, obtained by mixing equal quantities of the dextro-acid and lævo-acid, can be resolved into its components: the latter, consisting only of one kind of molecules, cannot be resolved. The rotation caused by the dextro-acid is equal in amount but opposite in sign to that due to the lævo-acid.

Emil Fischer has introduced a simple mode of writing the spacial formulæ of optically active compounds, of which frequent use will be made later. The representation in space of two C-atoms in union, in a compound $\begin{array}{l}\mathrm{C}abc\\ |\\ \mathrm{C}abc\end{array}$, is shown in Fig. 58 (169).

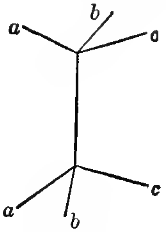


FIG. 58.

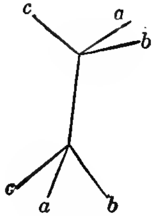
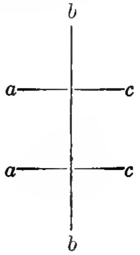
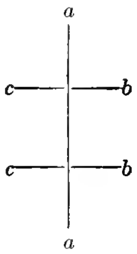


FIG. 59.

If the two bonds uniting the two carbon atoms are supposed to lie in the plane of the paper, then the positions of *a* and *c* are to the back, and of *b* to the front. If *a*, *b*, and *c* are imagined to be projected upon the plane of the paper, and *a* and *c* simultaneously so altered in position that they lie in the same straight line at right angles to the vertical axis, and *b* lies in this axis produced, then projection-figure I. is obtained:



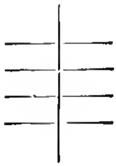
I.



II.

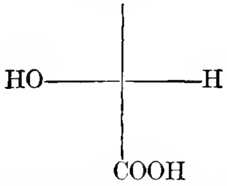
If Fig. 58 is rotated round its vertical axis, so that *a*, for example, lies in front of the plane of the paper, Fig. 59 results, its projection being represented by II. These apparently different configurations are identical.

For a chain of four carbon atoms there is obtained analogously the projection-figure



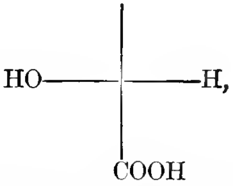
This will be understood if it is imagined that the figures in 169 (Fig. 33) are so placed that the plane in which the carbon bonds lie is at right angles to that of the paper, and the figures in this position are projected in the manner just described.

The projection-formulæ for the four isomeric tartaric acids are thus obtained. If the projection-figure for two asymmetric C-atoms is divided in the middle of the vertical line, and the upper half of the figure rotated through 180° in the plane of the paper, the similar grouping of HO, H, and COOH about the asymmetric C-atoms in both halves,



$$\begin{array}{ccc} & | & \\ \mathrm{HO} & - & \mathrm{H} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

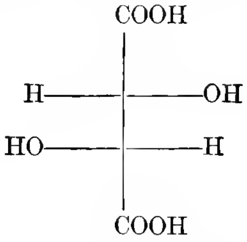
and



$$\begin{array}{ccc} & | & \\ \mathrm{HO} & - & \mathrm{H}, \\ & | & \\ & \mathrm{COOH} & \end{array}$$

indicates that both C-atoms rotate the plane of polarization in the same direction. We shall arbitrarily assume that this grouping occasions dextro-rotation.

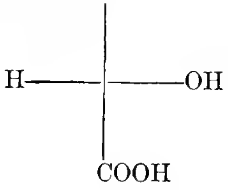
When the two carbon atoms are again united by transposing one of the halves in the plane of the paper, the figure



$$\begin{array}{ccc} & \mathrm{COOH} & \\ & | & \\ \mathrm{H} & - & \mathrm{OH} \\ \mathrm{HO} & - & \mathrm{H} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

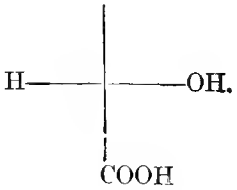
results, and is therefore the projection-formula for the dextro-rotatory acid.

The grouping with respect to the two C-atoms in the lævo-rotatory acid must be the mirror-image of that in the dextro-rotatory (52): thus,



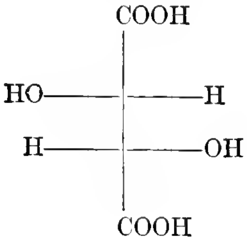
$$\begin{array}{ccc} & | & \\ \mathrm{H} & - & \mathrm{OH} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

and



$$\begin{array}{ccc} & | & \\ \mathrm{H} & - & \mathrm{OH}. \\ & | & \\ & \mathrm{COOH} & \end{array}$$

The combination of these two gives the projection-formula

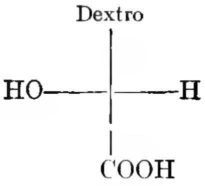


$$\begin{array}{c}COOH\\ HO-\!\!-C-\!\!-H\\ H-\!\!-C-\!\!-OH\\ COOH\end{array}$$

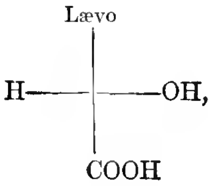
for the lævo-rotatory acid.

These representations of the constitutions of dextro-tartaric acid and lævo-tartaric acid cannot be made to coincide by altering their position in the plane of the paper,* and are therefore different.

When the acid contains a dextro-rotatory and a lævo-rotatory C-atom, as in mesotartaric acid, the arrangement of the groups will be

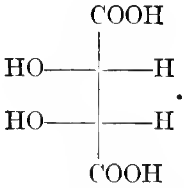


$$\begin{array}{c}HO-\!\!-C-\!\!-H\\ COOH\end{array}$$



$$\begin{array}{c}H-\!\!-C-\!\!-OH,\\ COOH\end{array}$$

and their projection-formula

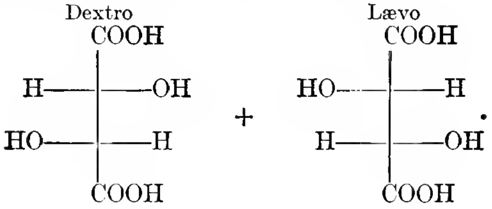


$$\begin{array}{c}COOH\\ HO-\!\!-C-\!\!-H\\ HO-\!\!-C-\!\!-H\\ COOH\end{array}$$

---

* These projection-formulæ can be made to coincide by rotating one of them through 180° about the line HO—H. It will be seen from a model, however, that the *spacial* formulæ cannot be made to coincide by this treatment. To determine by means of projection-formulæ whether this is possible for spacial formulæ, it is only admissible to transpose them in the plane of the paper.

The projection-formula for racemic acid is



Dextro-tartaric Acid.

192. *Potassium hydrogen* d-*tartrate*, $C_4H_5O_6K$, is present in the juice of grapes, and during alcoholic fermentation is deposited on the bottom of the casks, being even more sparingly soluble in dilute alcohol than in water. The crude product is called "argol"; when purified, it is known as "cream of tartar." To obtain *dextro-tartaric acid*, the crude argol is boiled with hydrochloric acid, and the acid precipitated as calcium tartrate, $CaC_4H_4O_6$, with milk of lime. After washing, the calcium salt is treated with an equivalent quantity of sulphuric acid, which precipitates calcium sulphate and sets free the tartaric acid: this can be obtained by evaporation in the form of large, transparent crystals, without water of crystallization, and having the composition $C_4H_6O_6$.

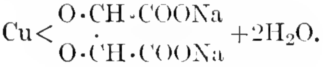
Dextro-tartaric acid melts at 170°, is very readily soluble in water, to a less extent in alcohol, and is insoluble in ether. When heated above its melting-point at atmospheric pressure, it loses water and yields various anhydrides, according to the intensity and duration of the heating. On stronger heating, it turns brown, with production of a caramel-like odour, and at a still higher temperature chars, with formation of pyroracemic and pyrotartaric acids. It can be converted into succinic acid by the action of certain bacteria.

In addition to the potassium hydrogen tartrate may be mentioned the *normal potassium salt*, $C_4H_4O_6K_2$, which is readily soluble in water, and *potassium antimonyl tartrate*,

$$2[COOK \cdot CHOH \cdot CHOH \cdot COO(SbO)] + H_2O.$$

On account of its medicinal properties, the latter is known as "tartar emetic." It is obtained by boiling potassium hydrogen tartrate with antimony oxide and water, and is readily soluble in water.

The precipitation of hydroxides from metallic salts—for example, copper hydroxide from copper sulphate—is prevented (161) by the presence of tartaric acid. The liquid obtained by dissolving copper sulphate, tartaric acid, and excess of caustic potash in water is called "FEHLING's solution." It is an important means of testing the reducing power of compounds, since reducing agents precipitate yellowish-red cuprous oxide, or its hydroxide, from the dark-blue solution. In this alkaline copper solution the hydroxyl-groups of the central C-atoms have reacted with the copper hydroxide, since one gramme-molecule of normal alkali tartrate can dissolve one gramme-molecule of copper hydroxide. These copper alkali tartrates have also been obtained in a crystalline form: thus, the compound $C_4H_2O_6Na_2Cu + 2H_2O$ is known, and must have the constitutional formula



$$Cu<\begin{matrix}O\cdot CH\cdot COONa\\ \cdot\\ O\cdot CH\cdot COONa\end{matrix} + 2H_2O.$$

Experiment has proved that in aqueous solution this compound is ionized to $Na^{\cdot}$ and the complex anion $Cu<\begin{matrix}O\cdot CH\cdot COO'\\ \cdot\\ O\cdot CH\cdot COO'\end{matrix}$. First, the reactions of the solution are no longer those of copper ions: although the liquid is alkaline, copper hydroxide is not precipitated. Second, on electrolysis the copper goes towards the anode. This has been studied by **KÜSTER** by the aid of the apparatus shown in Fig. 60. One U-tube contains copper-sulphate solution at *b*; the other, **FEHLING**'s solution at *d*: into both limbs of each is then carefully poured a solution of sodium sulphate, *a* and *c*. The common surfaces of the sodium-sulphate and copper-sulphate solutions in the two U-tubes lie in the same horizontal plane. When an electric current is passed through the tubes, preferably arranged in parallel,

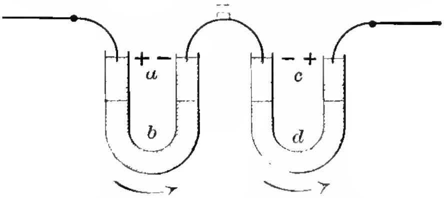


FIG. 60.—ELECTROLYSIS OF AN ALKALINE COPPER SOLUTION.

and not in series, a different effect is produced on the level of the surfaces of the copper solutions in each tube. In the copper-sulphate solution a rise takes place at the cathode, since the Cu-ions are cathions, and tend towards the cathode. The reverse effect is observed in the FEHLING'S solution, indicating that in it the copper is a constituent of the anion. The arrows in the figure show the direction in which the ions in each solution tend.

Moreover, the colour of FEHLING'S solution is a much more intense blue than that of a copper-sulphate solution of equivalent concentration, this being evidence of the presence in FEHLING'S solution of a complex ion containing copper.

FEHLING'S solution decomposes gradually, so that it is best prepared as required. OST has discovered a much more stable alkaline copper solution, applicable to the same purposes as that of FEHLING. It is a mixture of copper sulphate with potassium hydrogen carbonate and potassium carbonate, and contains a soluble double carbonate of copper and potassium.

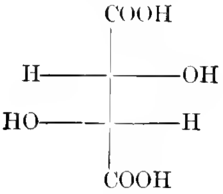
Lævo-tartaric Acid.

Lævo-tartaric acid is obtained from racemic acid. With two exceptions, the properties of the lævo-acid and its salts are identical with those of the dextro-modification and its salts. First, their rotatory power is equal, but opposite in sign: second, the salts formed by the lævo-acid with the optically active alkaloids differ in solubility from those derived from the dextro-acid (196).

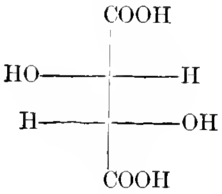
Racemic Acid.

193. It is stated in 186 that optically active substances can be converted by the action of heat into optically inactive compounds; that is, changed into a mixture of the dextro-modification and lævo-modification in equal proportions. This change is often facilitated by the presence of certain substances: thus, dextro-tartaric acid is readily converted into *racemic acid* by boiling with excess of a concentrated solution of caustic soda. Mesotartaric acid is simultaneously formed (194).

The optical inactivity is occasioned by conversion of one half of the dextro-acid into the lævo-modification. If formula I. represents the dextro-acid, then formula II. will correspond with the lævo-acid; and the formulæ indicate that the exchange of groups, by which an active compound is converted into its optical isomeride (186), must in this instance take place at both asymmetric C-atoms, in order that the dextro-acid may yield its lævo-isomeride.



I.



II.

Racemic acid is not so soluble in water as the two optically active acids, and differs in crystalline form from them: the crystals have the composition $2C_4H_6O_6 + 2H_2O$. In many of its salts the amount of water of crystallization differs from that in the corresponding optically active salts. Racemic acid is proved to consist of two components by its synthesis from solutions of the dextro-acid and the lævo-acid. If the solutions are concentrated, heat is developed on mixing, and the less soluble racemic acid crystallizes out. Racemic acid can also be resolved into the two optically active modifications (196).

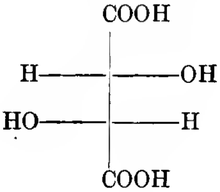
Although racemic acid in the solid state differs from both dextro-tartaric acid and lævo-tartaric acid, yet in solution, or as ester in the state of vapour, it is only a mixture of them. The cryoscopic depression produced by it corresponds with the molecular formula $C_4H_6O_6$; and the vapour-density of its ester to single, instead of to double, molecules.

The term "racemic" is applied to substances which consist of isomerides of equal and opposite rotatory power in equimolecular proportions, and are therefore optically inactive. This phenomenon was first observed by Pasteur in his researches on racemic acid (196).

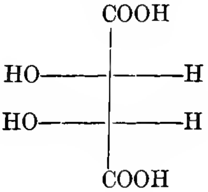
Mesotartaric Acid.

194. Like racemic acid, *mesotartaric acid* is optically inactive, but cannot be resolved into optically active components. It is formed when dextro-tartaric acid is boiled for several hours under a reflux-condenser with a large excess of caustic soda (193).

If formula I. is assigned to dextro-tartaric acid, it is evident that to convert it into mesotartaric acid, formula II., it is only necessary



I.



II.

for two groups in union with a single asymmetric C-atom to change places, while racemic acid can only result through exchange of the

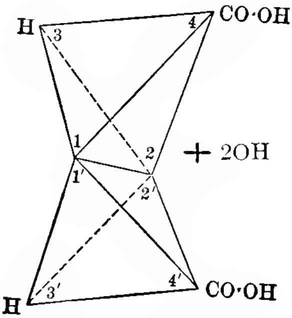
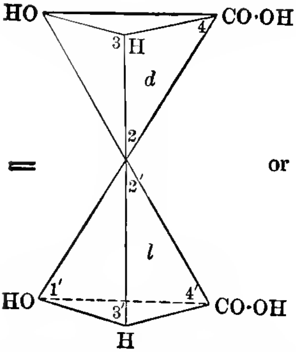


Fig. 61.—Maleïc Acid.



or

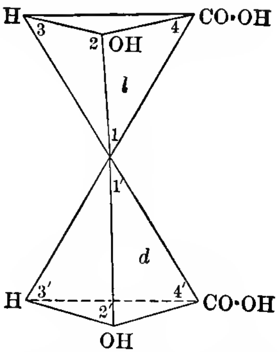


Fig. 62.—Mesotartaric Acid. Fig. 63.—Mesotartaric Acid.

groups linked to both C-atoms. This affords an explanation of the fact that when dextro-tartaric acid is heated with dilute hydrochloric acid, or boiled with dilute caustic soda, mesotartaric acid is first formed, and racemic acid only after prolonged heating.

Potassium hydrogen mesotartrate is readily soluble in cold water, differing in this from the corresponding salts of the other tartaric acids.

195. This view of the structure of the tartaric acids is in complete accord with their relation to fumaric acid and maleïc acid (170), which, on treatment with a dilute aqueous solution of potassium permanganate, yield respectively racemic acid and mesotartaric acid by addition of two hydroxyl-groups. Addition of 2OH to maleïc acid may result from the severance of the bond 1:1′ or 2:2′ in Fig. 61, with production of the configurations represented in Figs. 62 and 63. The projection-formulæ corresponding to Figs. 62 and 63 are

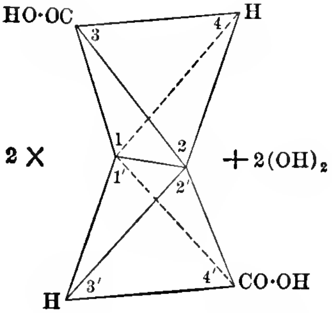


FIG. 64.—FUMARIC ACID.

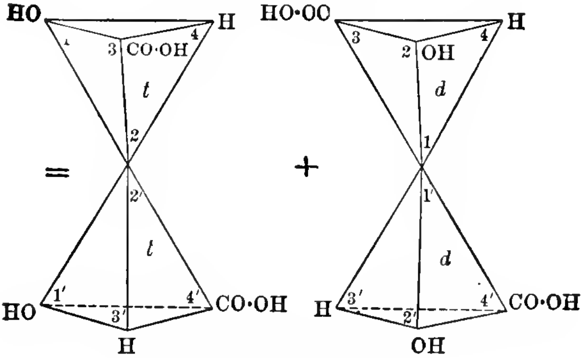
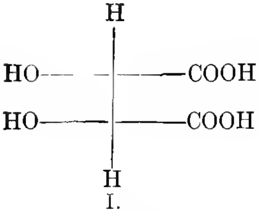
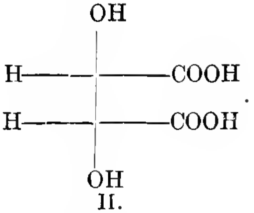


FIG. 65.—RACEMIC ACID.



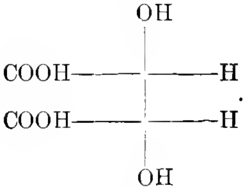
I.

and



II.

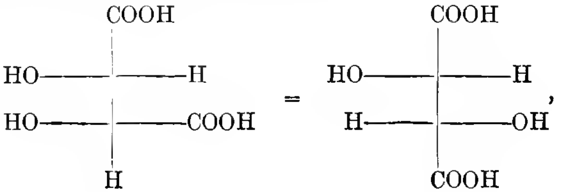
These apparently different configurations are identical, as becomes evident on rearranging I. (p. 233):

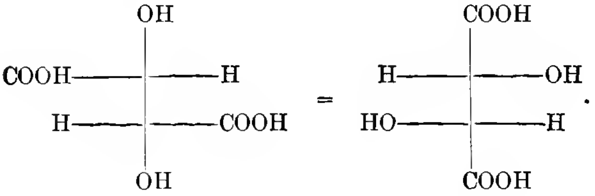


If the last projection-formula is rotated in the plane of the paper through 180°, it will coincide with II. A comparison of this scheme with that in 194 shows it to be the configuration representing mesotartaric acid. It follows that addition of two hydroxyl-groups to maleïc acid produces only mesotartaric acid.

A different result is obtained by addition of two OH-groups to fumaric acid, as is indicated by Figs. 64 and 65.

Severance of the bonds 1:1′ or 2:2′ by addition yields two configurations which cannot be made to coincide by rotation. This is made clearer by the projection-formulæ





These projection-formulæ are identical with the configurations representing dextro-tartaric and lævo-tartaric acid (p. 236).

Racemic Substances, and their Resolution into Optically Active Constituents.

196. Optically active isomerides display no difference in their physical or in their chemical properties, except the rotation of the plane of polarized light in opposite directions, and certain physiological effects not yet explained. They have, therefore, the same solubility, boiling-point, and melting-point; their salts crystallize with the same number of molecules of water of crystallization; and so on. It follows that the resolution of an optically inactive substance into its optically active components cannot be effected by the ordinary methods, since these are based on differences in physical properties.

PASTEUR has devised three methods for effecting this resolution. The first depends upon the fact that racemates sometimes crystallize from solution in two forms, one corresponding to the dextro-salt, and the other to the lævo-salt: these can be mechanically separated. PASTEUR effected this for sodium ammonium racemate, $C_8H_8O_{12}Na_2(NH_4)_2+2H_2O$. Later, VAN 'T HOFF proved that crystals of the dextro-tartrate and lævo-tartrate are only obtained from this solution at temperatures below 28°, the transition-point for these salts ("Inorganic Chemistry," **70**):

$$\underset{\text{Dextro-}+\text{lævo- Na-NH}_4\text{-tartrate}}{2Na(NH_4)C_4H_4O_6\cdot 4H_2O} \rightleftarrows \underset{\text{Na-NH}_4\text{-racemate}}{C_8H_8O_{12}Na_2(NH_4)_2\cdot 2H_2O} + 6H_2O.$$

Fig. 66 represents the crystal-forms of the two tartrates, the difference between them being due to the positions of the planes *a* and *b*. The crystal-forms are mirror-images, and cannot be made to coincide.

Sometimes separation can be effected by inoculating a supersaturated solution of the racemic compound with a crystal of another substance isomorphous with only one of the components. By thus inoculating a supersaturated solution of sodium ammonium racemate with *l*-asparagine (**231**), VON OSTROMISSLENSKY isolated sodium ammonium dextro-tartrate in crystalline form.

Pasteur's second method of resolution depends upon a difference in solubility of the salts formed by the union of optically active acids with optically active bases. When a dextro-acid or a lævo-acid is united with an optically inactive base, as in the metallic salts, the internal structure of the molecule remains unchanged: the constitution of the salt-molecules, like that of the free acids, can be represented by configurations which are mirror-images. But it is otherwise when the dextro-acid and the lævo-acid are united with an optically active (for example, a dextro-rotatory) base: the configurations of the salt-molecules are then no longer mirror-images, and identity of physical properties must of necessity cease.

Racemic acid can be thus resolved by means of its cinchonine salt, since cinchonine lævo-tartrate is less soluble than the dextro-tartrate, and crystallizes out from solution first. Strychnine can be advantageously employed in the resolution of lactic acid, and other similar examples might be cited.

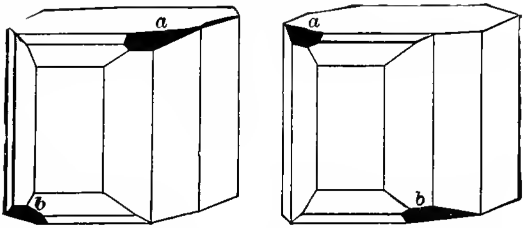


Fig. 66.—Crystal-forms of the Sodium Ammonium Tartrates.

The conversion of enantiomorphic isomerides into derivatives with configurations which are no longer mirror-images of one another can be otherwise effected: thus, for acids, by the formation of an ester with an optically active alcohol. The velocity of ester-formation with an optically inactive alcohol must be the same for both isomerides, on account of the perfectly symmetrical structure of the esters formed; but with an optically active alcohol the two isomerides are not esterified at the same rate, since the compounds formed are no longer mirror-images of one another. Marckwald found that when racemic mandelic acid (**391**, 3) is heated for one hour at 155° with menthol (**412**), an active alcohol, the non-esterified acid is lævo-rotatory.

The third method of fission devised by Pasteur depends on the action of mould-fungi (*Penicillium glaucum*), or of bacteria. Thus, when racemic lactic acid in very dilute solution is treated with the *Bacillus acidi lævolactici*, after addition of the necessary nutriment for the bacteria, the optically inactive solution becomes lævo-rotatory, since only the dextro-rotatory acid is converted by the bacilli into other substances. A dilute solution of racemic acid, into which traces of the mould-fungus *Penicillium glaucum* have been introduced, becomes lævo-rotatory, the fungus propagating itself with decomposition of the dextro-rotatory acid.

The second and third methods of resolution are alike in principle. During their growth the bacteria and fungi develop substances called enzymes (**219**), which decompose compounds by means hitherto unexplained. These enzymes are optically active; hence, a difference in their action on the optical isomerides, analogous to that described in the previous paragraph, is to be expected.

197. When a racemic substance is liquid or gaseous, it consists only of a mixture of the two enantiomorphic isomerides: an example of this is afforded by racemic acid in solution and in the form of esters (**193**). If the substance is crystalline, there are three possibilities.

First, the individual crystals may be dextro-rotatory or lævo-rotatory, so that the two modifications can be mechanically separated. This is expressed by the statement that the racemic substance is a *conglomerate* of the isomerides.

Second, it may be a true compound of the dextro-modification and lævo-modification, a *racemic* compound or *racemoid*, its formation being comparable to that of a double salt, when a solution containing two salts is allowed to crystallize under certain conditions.

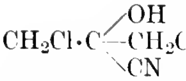
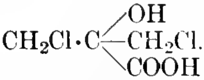
The third possibility is also analogous to the crystallization of salt-solutions, whereby crystals are sometimes obtained containing both salts, but in proportions varying in different crystals. It sometimes happens that the salts crystallize together in all proportions, but usually these can vary only between certain limits. This simultaneous crystallization of salts yields the so-called *mixed crystals;* and optical isomerides produce *pseudoracemic* mixed crystals.

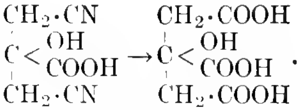
The variety of crystals obtained from a given solution or fused mass of a racemic substance—a conglomerate, a racemic compound, or pseudoracemic mixed crystals—depends upon the temperature of crystallization, and upon other conditions. An example of this is afforded by sodium ammonium racemate (**196**): when concentrated above 28° the racemate crystallizes from the solution of this salt; below this temperature a mixture of the individual tartrates —the conglomerate—is obtained.

Bakhuis Roozeboom has indicated a method of distinguishing between these three classes of compounds. For a conglomerate, this is simple. A saturated solution is made: it must be optically inactive, and saturated alike for the dextro-rotatory and for the lævo-rotatory body. If now the solid dextro-compound or lævo-compound is added, and the mixture agitated, nothing more will dissolve, the liquid being already saturated with respect to the two isomerides: the amount of dissolved substance is still the same, and the solution remains optically inactive. On the other hand, if a racemic compound was present, although the solution was saturated in the first instance with regard to this, it is unsaturated with respect to the two optically active modifications: addition of the solid dextro-rotatory or lævo-rotatory substance will cause a change in the total quantity of solid dissolved, and the liquid will become optically active. Less simple methods are sometimes necessary to detect pseudoracemic mixed crystals.

IV. POLYBASIC HYDROXY-ACIDS.

198. Of these acids it will be sufficient to describe the tribasic *citric acid*, $C_6H_8O_7$, which is widely distributed in the vegetable kingdom, and is also found in cows' milk. It is prepared from the juice of unripe lemons, which contains 6–7 per cent. Tricalcium citrate dissolves readily in cold water, but very slightly in boiling water: this property is employed in the separation of the acid from lemon-juice, it being obtained in the free state by addition of sulphuric acid to the citrate. Another technical method for its preparation depends upon the fact that certain mould-fungi (*Citromyces pfefferianus* and *C. glaber*) produce considerable quantities of citric acid from dextrose or sucrose.

Citric acid can be obtained synthetically by a method proving its constitution. On oxidation, symmetrical dichlorohydrin, $CH_2Cl \cdot CHOH \cdot CH_2Cl$ (**162**), is transformed into symmetrical dichloroacetone, $CH_2Cl \cdot CO \cdot CH_2Cl$. The cyanohydrin-synthesis converts this into  $CH_2Cl\cdot C\begin{array}{l}\diagup OH\\ -CH_2Cl\\ \diagdown CN\end{array}$, and hydrolysis yields the hydroxy-acid,  $CH_2Cl\cdot C\begin{array}{l}\diagup OH\\ -CH_2Cl\\ \diagdown COOH\end{array}$. On treatment of this compound with potassium cyanide, a dicyanide is formed, which can be hydrolyzed to citric acid:



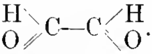
$$\begin{array}{l}CH_2\cdot CN\\ \;|\\ C<\begin{array}{l}OH\\COOH\end{array}\\ \;|\\ CH_2\cdot CN\end{array}\rightarrow\begin{array}{l}CH_2\cdot COOH\\ \;|\\ C<\begin{array}{l}OH\\COOH\end{array}\\ \;|\\ CH_2\cdot COOH\end{array}.$$

The alcoholic character of citric acid is indicated by the formation of an acetyl-compound from triethyl citrate and acetyl chloride.

Citric acid forms well-defined crystals containing one molecule of water of crystallization, and is readily soluble in water and alcohol. It loses its water of crystallization at 130°, and melts at 153°. It is employed in the manufacture of lemonade, and in calico-printing.

DIALDEHYDES AND DIKETONES: HALOGEN-SUBSTITUTED ALDEHYDES AND KETONES.

Dialdehydes.

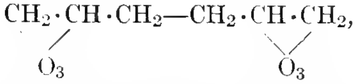
199. The simplest member of the series of dialdehydes, *glyoxal*, is a combination of two aldehydo-groups,  $\begin{matrix}H\\O\end{matrix}\!\!>C{-}C<\!\!\begin{matrix}H\\O\end{matrix}$. It is best prepared by carefully floating a layer of water on the surface of strong nitric acid contained in a tall glass cylinder, and pouring ethyl alcohol on the surface of the water, care being taken that the layers do not mix. The nitric acid and alcohol diffuse into the water; and the alcohol is slowly oxidized to glyoxal, glycollic acid, oxalic acid, and other substances.

Thus prepared, glyoxal is a colourless, amorphous substance: when moist, it dissolves readily in water, but very slowly after complete drying *in vacuo* at 110°–120°. It is a polymeride of unknown molecular weight, although its aqueous solution reacts as though it contained only simple molecules. Distillation of this polymeride with phosphoric anhydride evolves an emerald-coloured gas, condensable by cooling to beautiful yellow crystals, which at a lower temperature become colourless. They melt at 15°, and the yellow liquid thus obtained boils at 51°. It is unimolecular glyoxal, and can only exist as such for a short time: traces of water readily polymerize it. The unimolecular form is the simplest type of coloured compound, containing only carbon, hydrogen, and oxygen.

The combination of glyoxal with two molecules of sodium hydrogen sulphite, and the formation of a dioxime, prove it to be a double aldehyde. It also has the other properties peculiar to aldehydes, such as the reduction of an ammoniacal silver solution with formation of a mirror. On oxidation, it takes up two atoms of oxygen, yielding oxalic acid, of which it is the dialdehyde. Treatment with caustic potash converts glyoxal into glycollic acid, one aldehydo-group being reduced and the other oxidized. This reaction may be explained by the assumption that an addition-product with water is formed, in accordance with the scheme

$$C^{H}_{O}\cdot C^{H}_{O} + H_2O = \underset{\text{Glycollic acid}}{CH_2OH\cdot COOH}.$$

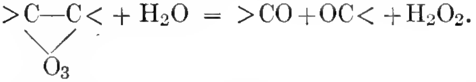
Succindialdehyde, ${}^{H}_{O}C\cdot CH_2\cdot CH_2\cdot C^{H}_{O}$, has been prepared by HARRIES by the action of ozone upon a chloroform solution of diallyl, $CH_2{:}CH\cdot CH_2—CH_2\cdot CH{:}CH_2$. An addition-product—a diozonide—is formed,



$$CH_2\cdot CH\cdot CH_2—CH_2\cdot CH\cdot CH_2, \quad O_3 \quad O_3$$

each double linking uniting with one molecule of ozone. This diozonide is a syrup-like, explosive liquid. When heated slowly with water, it decomposes, forming succindialdehyde.

HARRIES has prepared several analogous ozonides, each double linking always taking up O_3. Water decomposes these ozonides in accordance with the scheme



$$>C—C< + H_2O = >CO + OC< + H_2O_2. \quad O_3$$

The formation of these ozonides and their decomposition by water afford an excellent method for determining the position in the molecule of double linkings. Its application to the case of oleïc acid has confirmed the formula indicated in 144.

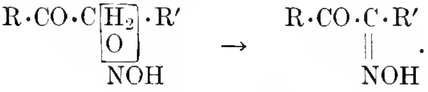
Diketones.

200. The diketones contain two carbonyl-groups: their properties and the methods employed in their preparation depend upon the relative position of these groups. 1:2-Diketones with the group $—\overset{1}{C}O\cdot\overset{2}{C}O—$ are known: 1:3-diketones with $—\overset{1}{C}O\cdot\overset{2}{C}H_2\cdot\overset{3}{C}O—$: 1:4-diketones with $—\overset{1}{C}O\cdot\overset{2}{C}H_2\cdot\overset{3}{C}H_2\cdot\overset{4}{C}O—$: and so on.

1:2-*Diketones* cannot be obtained by the elimination of chlorine from the acid chlorides by the action of a metal, in accordance with the scheme

$$R\cdot CO\boxed{Cl+Na_2+Cl}OC\cdot R.$$

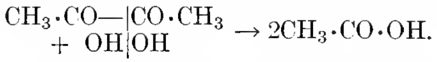
Their preparation is effected by the action of amyl nitrite and a small proportion of hydrochloric acid on a ketone, one of the CH_2-groups being converted into $C{=}NOH$:



$$\begin{array}{l}R\cdot CO\cdot C\boxed{H_2}\cdot R' \\ \qquad\quad\;\boxed{O} \\ \qquad\quad\; NOH\end{array} \quad\rightarrow\quad \begin{array}{c}R\cdot CO\cdot C\cdot R'\\ \| \\ NOH\end{array}.$$

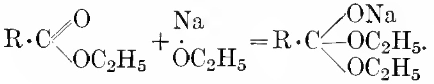
These compounds are called *isonitrosoketones*. When boiled with dilute sulphuric acid, the oxime-group is eliminated as hydroxylamine, with formation of the diketone. The *ketoaldehydes* are both ketones and aldehydes, and contain the group $-CO\cdot C\begin{cases}H\\O\end{cases}$: they, too, can be obtained by this method.

Diacetyl, $CH_3\cdot CO\cdot CO\cdot CH_3$, can be prepared from methylethylketone in the manner indicated. It is a yellow liquid of pungent, sweetish odour, and is soluble in water: its vapour has the same colour as chlorine. Diacetyl boils at 88°, and has a specific gravity of 0·973 at 20°. Its behaviour points to the presence of two carbonyl-groups in the molecule: thus, it adds on 2HCN, yields a mono-oxime and a dioxime, and so on. The adjacency of the two carbonyl-groups in diacetyl is proved by its quantitative conversion into acetic acid under the influence of hydrogen peroxide:



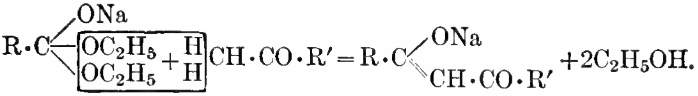
$$\begin{array}{l}CH_3\cdot CO-|CO\cdot CH_3 \\ \qquad\;\; +\; OH|OH\end{array} \rightarrow 2CH_3\cdot CO\cdot OH.$$

1:3-*Diketones* can be prepared by a condensation-method of general application discovered by Claisen and Wislicenus. Sodium ethoxide is the condensing agent. An addition-product is formed by the interaction of this substance and an ester:



$$R\cdot C\begin{cases}O\\OC_2H_5\end{cases} + \overset{Na}{\dot{O}}C_2H_5 = R\cdot C\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases}.$$

The addition-product is then brought into contact with a ketone $R'\cdot CO\cdot CH_3$, two molecules of alcohol being eliminated with formation of a condensation-product:



$$R\cdot C\begin{array}{l}\nearrow ONa\\ -\boxed{\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}+\begin{array}{l}H\\H\end{array}}CH\cdot CO\cdot R'\\ \searrow\end{array} = R\cdot C\begin{array}{l}\nearrow ONa\\ \searrow CH\cdot CO\cdot R'\end{array} + 2C_2H_5OH.$$

On treatment of this compound with a dilute acid, the sodium atom is replaced by hydrogen. This might produce a compound with a hydroxyl-group attached to a doubly-linked carbon atom; but usually compounds of this type are unstable, the group $-\overset{OH}{\dot{C}}{=}CH-$ changing to $-CO-CH_2-$. The principle applies in the present instance, $R\cdot\overset{OH}{\dot{C}}{=}CH\cdot CO\cdot R'$ yielding a 1:3-diketone, $R\cdot CO-CH_2-CO\cdot R'$.

Claisen has found that sodamide, $Na\cdot NH_2$, can be substituted advantageously for sodium ethoxide in the condensation of ketones with esters. Frequently, it not only facilitates the reaction, but increases the yield.

Another method for the preparation of 1:3-diketones is the action of acid chlorides on the sodium compounds of acetylene homologues:

$$\underset{\text{Sodio-}n\text{-amylacetylene}}{CH_3\cdot(CH_2)_4\cdot C{\equiv}C}\boxed{Na+Cl}\underset{\text{Acetyl chloride}}{OC\cdot CH_3} \rightarrow CH_3\cdot(CH_2)_4\cdot C{\equiv}C\cdot CO\cdot CH_3.$$

By treating this ketone with concentrated sulphuric acid, water is added, and the desired diketone obtained:

$$CH_3\cdot(CH_2)_4\cdot C{\equiv}C\cdot CO\cdot CH_3 = CH_3\cdot(CH_2)_4\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$
$$+ \quad O \quad H_2$$

These diketones have a weak acidic character, their dissociation-constants being very small. Among others, that of *acetylacetone*, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$, has been determined. They contain two H-atoms replaceable by metals. These must belong to the methylene-group between two negative carbonyl-groups; for if the other hydrogen atoms could be thus exchanged for metals, there is no reason, since they are of equal value, that two, and only two, should be replaceable.

Acetylacetone is obtained by the condensation of ethyl acetate and acetone. It is a colourless liquid of agreeable odour, boils at 137°, and has a specific gravity of 0·979 at 15°. When boiled with water, it decomposes into acetone and acetic acid, a reaction affording another example of the instability of compounds containing a carbon atom loaded with negative groups.

Among the salts of acetylacetone is the copper salt, $(C_5H_7O_2)_2Cu$, which is sparingly soluble in water; and the volatile aluminium salt, $(C_5H_7O_2)_3Al$. By a determination of the vapour-density of this compound, Combes has shown that the aluminium atom is tervalent.

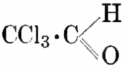
These metallic compounds have properties differing from those of ordinary salts. Unlike true salts, they are soluble in benzene, chloroform, and other organic solvents. Their aqueous solutions are almost non-conductors of electricity. They either do not answer to the ordinary tests for the metals, or else react very slowly. The ferric and aluminium salts, in which both base and acid are very weak, do not undergo hydrolytic dissociation, but diffuse unchanged through parchment-paper. In these respects they resemble mercuric cyanide ("Inorganic Chemistry," 274), which is practically not ionized in aqueous solution, and therefore lacks all the properties characteristic of ordinary salts.

A type of the 1:4-*diketones* is *acetonylacetone*,

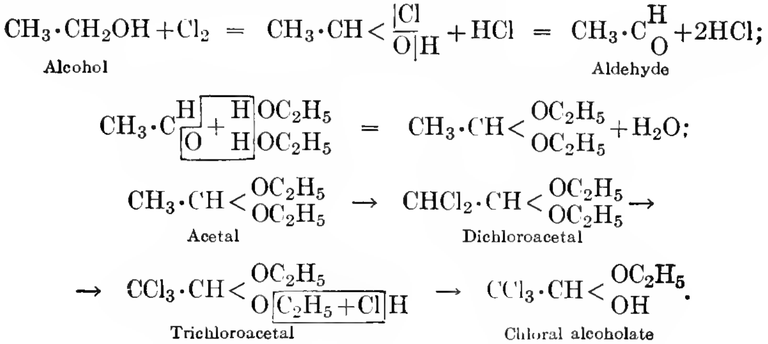
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3,$$

the preparation of which is described in 251. It is a colourless liquid of agreeable odour: it boils at 193°, and has a specific gravity of 0·970 at 21°. Acetonylacetone and other 1:4-diketones yield cyclic compounds, which are dealt with in 457–460.

Halogen-substituted Aldehydes.

201. *Chloral* or trichloroacetaldehyde,  $CCl_3{\cdot}C\begin{smallmatrix}\diagup H\\ \diagdown\!\!\diagdown O\end{smallmatrix}$, is of great therapeutic importance, since with one molecule of water it forms a crystalline compound known as *chloral hydrate*, and employed as a soporific. Chloral is technically prepared by saturating ethyl alcohol with chlorine. The alcohol must be as free from water as possible, and the chlorine carefully dried. At first the reaction-mixture is artificially cooled, but after a few days the process becomes less energetic, and the temperature is slowly raised to 60°, and finally to 100°.

The reaction may be explained by assuming that the alcohol is first converted into aldehyde, which is then transformed into acetal, dichloroacetal, and trichloroacetal: the last compound is converted, by the hydrochloric acid produced, into *chloral alcoholate*, $CCl_3\cdot CH<\begin{matrix}OC_2H_5\\OH\end{matrix}$. Dichloroacetal and other intermediate products of this reaction have been isolated:



$$\underset{\text{Alcohol}}{CH_3\cdot CH_2OH}+Cl_2 = CH_3\cdot CH<\begin{matrix}|Cl\\O|H\end{matrix}+HCl = \underset{\text{Aldehyde}}{CH_3\cdot C\begin{matrix}H\\O\end{matrix}}+2HCl;$$

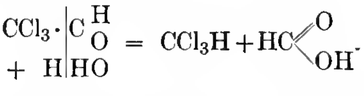
$$CH_3\cdot C\boxed{\begin{matrix}H\\O\end{matrix}+\begin{matrix}H\\H\end{matrix}}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} = CH_3\cdot CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}+H_2O;$$

$$\underset{\text{Acetal}}{CH_3\cdot CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}} \rightarrow \underset{\text{Dichloroacetal}}{CHCl_2\cdot CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}} \rightarrow$$

$$\rightarrow \underset{\text{Trichloroacetal}}{CCl_3\cdot CH<\begin{matrix}OC_2H_5\\O\boxed{C_2H_5+Cl}H\end{matrix}} \rightarrow \underset{\text{Chloral alcoholate}}{CCl_3\cdot CH<\begin{matrix}OC_2H_5\\OH\end{matrix}}.$$

The final product of chlorination is a crystalline mixture of chloral alcoholate, chloral hydrate, and trichloroacetal, from which chloral is obtained by treatment with concentrated sulphuric acid. It is an oily liquid of penetrating odour, boiling at 97°, and having a specific gravity of 1·512 at 20°. When treated with water, it is converted with evolution of heat into the well-crystallized chloral hydrate. To this compound is assigned the formula $CCl_3\cdot CH<\begin{matrix}OH\\OH\end{matrix}$, as it does not show all the aldehyde-reactions. For example, it does not restore the red tint of a solution of magenta (**425**) which has been decolorized with sulphurous acid (**116**, 3). Chloral hydrate is, therefore, one of the few known compounds containing two OH-groups in union with a single C-atom (**249** and **253**).

Otherwise, chloral behaves as an aldehyde: for instance, it reduces an ammoniacal silver solution with formation of a mirror, and is oxidized by nitric acid to trichloroacetic acid. Solutions of the alkalis decompose it at ordinary temperatures with formation of chloroform and formic acid:



$$\begin{matrix}CCl_3\cdot\\+\ H\end{matrix}\left|\begin{matrix}C\begin{matrix}H\\O\end{matrix}\\HO\end{matrix}\right. = CCl_3H+HC\begin{matrix}\nearrow O\\\searrow OH\end{matrix}.$$

On account of its purity, chloroform prepared in this manner is preferred for pharmaceutical use.

The formation of chloroform from chloral by the action of alkaline liquids originally suggested the use of chloral as a soporific: it was expected that the alkaline constituents of the blood would decompose it with the formation of chloroform in the body itself. Liebreich showed that chloral has in fact a soporific action, but more recent investigation has proved this to be independent of the formation of chloroform, since the chloral is eliminated from the system as a complicated derivative, *urochloralic acid.*

Halogen-substituted Ketones.

202. An example of this class of compounds, dichloroacetone, $CH_2Cl \cdot CO \cdot CH_2Cl$, is mentioned in 198. Variously substituted ketones, some of which have a powerful odour, are obtained from acetone by direct chlorination.

ALDEHYDO-ALCOHOLS AND KETO-ALCOHOLS OR SUGARS.

203. Aldehydo-alcohols and keto-alcohols are natural products, and are very widely distributed. They are called *carbohydrates*, *sugars*, or *saccharides*. They contain one carbonyl-group and several hydroxyl-groups. *One of the hydroxyl-groups must be linked directly to a carbon atom in union with the carbonyl-group, so that* the characteristic group of these compounds is —CHOH—CO—.

The sugars are classified as *polyoses* and *monoses*. On hydrolysis, the polyoses yield monoses, which have lower molecular weights than their parent substances, but possess all the properties characteristic of the sugars. The monoses do not admit of further hydrolysis to simpler sugars. They will be considered first.

Nomenclature and General Properties of the Monoses and their Derivatives.

204. When the monoses are aldehydes they are called *aldoses*, and when ketones, *ketoses*. The number of carbon atoms in the molecule is indicated by their names: thus, *pentose*, *hexose*, *heptose*, etc. To distinguish between aldoses and ketoses the prefixes "aldo-" and "keto-" respectively are used; as *aldohexose*, *keto-hexose*, and so on.

When the polyoses may be regarded as derived from two monose molecules by the elimination of one molecule of water, they are called *dioses;* thus, *hexodioses* when they are formed from two molecules of hexose. The polyoses derived from three monose molecules by the elimination of two molecules of water are called *trioses;* as *hexotriose*, etc.

Like other aldehydes, the aldoses are converted by oxidation into monobasic acids containing the same number of carbon atoms, the pentoses yielding the monobasic *pentonic acids*, the hexoses the *hexonic acids*, etc. The oxidation can be carried further; for the general formula of an aldose is $CH_2OH\cdot(CHOH)_n\cdot C\begin{smallmatrix}\diagup H\\ \diagdown O\end{smallmatrix}$ (206), and the group $—CH_2OH$ can be oxidized to carboxyl, yielding a dibasic acid containing the same number of carbon atoms as the aldose from which it is derived. On oxidation, the ketoses yield acids containing a smaller number of carbon atoms.

On reduction, the aldoses and ketoses take up two hydrogen atoms, with formation of the corresponding alcohols: thus, hexose yields a *hexahydric alcohol*, and pentose a *pentahydric alcohol* (206 and 208).

205. Four reactions are known which are characteristic of all monoses: two of these they possess in common with the aldehydes (116).

1. They reduce an ammoniacal silver solution on warming, forming a metallic mirror.

2. When warmed with alkalis, they give a yellow, and then a brown, coloration, and ultimately resinify.

3. When an alkaline copper solution (Fehling or Ost, 192) is heated with a solution of a monose, reduction takes place, with formation of yellow-red suboxide of copper.

4. When a monose is heated with excess of phenylhydrazine, $C_6H_5\cdot NH\cdot NH_2$, in dilute acetic-acid solution, a yellow compound, crystallizing in fine needles, is formed: substances of this type are insoluble in water, and are called *osazones*. Their formation may be explained as follows.

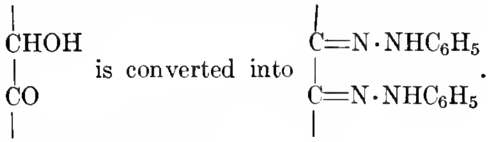
It is mentioned in 203 that the sugars are characterized by containing the group —CHOH—CO—. The action of phenylhydrazine on a carbonyl-group has already been explained (112); water is eliminated, and a hydrazone formed:

$$\begin{array}{c}|\\ C\\ |\end{array}\boxed{O+H_2}N\cdot NHC_6H_5 = \begin{array}{c}|\\ C\\ |\end{array}:N\cdot NHC_6H_5+H_2O.$$

A second molecule of phenylhydrazine then reacts with the group —CHOH—, from which two hydrogen atoms are eliminated, the molecule of phenylhydrazine being decomposed into ammonia and aniline:

$$\underset{\text{Phenylhydrazine}}{C_6H_5\cdot NH\cdot NH_2} = \underset{\text{Aniline}}{C_6H_5\cdot NH_2} + NH_3.$$
$$+ \quad H\ H$$

The elimination of two hydrogen atoms from the group —CHOH— converts it into a carbonyl-group, —CO—, with which a third molecule of phenylhydrazine reacts, forming a hydrazone, so that



$$\text{the group } \begin{array}{l} | \\ CHOH \\ | \\ CO \\ | \end{array} \text{ is converted into } \begin{array}{l} | \\ C{=}N\cdot NHC_6H_5 \\ | \\ C{=}N\cdot NHC_6H_5 \\ | \end{array}.$$

This group is characteristic of the osazones.

The osazones dissolve in water with difficulty. This property makes them of service in the separation of the monoses, which are very soluble in water, and crystallize with great difficulty, especially in presence of salts, and hence often cannot be purified by crystallization. By means of the sparingly soluble osazones, however, they can be separated: the osazones are readily obtained in the pure state by crystallization from a dilute solution of pyridine (449). Moreover, the identity of the monose can be established by a determination of the melting-point of the osazone obtained from it.

Constitution of the Monoses.

206. It is shown later that the constitution of all the monoses follows from that of the aldohexoses, the structure of which can be arrived at as follows:

1. The aldohexoses have the molecular formula $C_6H_{12}O_6$.

2. The aldohexoses are aldehydes, and, therefore, contain a carbonyl-group in the molecule. This follows from the facts that they show the reactions characteristic of aldehydes; that they are converted by oxidation into acids containing the same number of C-atoms, and by reduction into an alcohol; and that they form addition-products with hydrocyanic acid.

3. All known hexoses contain a normal chain of six carbon atoms, since they can be reduced to a hexahydric alcohol, which,

on further reduction at a high temperature with hydriodic acid, yields *n*-secondary hexyl iodide, $CH_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$.

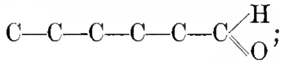
> The constitution of this iodide is inferred from the fact that it can be converted into an alcohol, which on oxidation yields
>
> $$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3;$$
>
> for on further oxidation this is converted into *n*-butyric acid and acetic acid.

4. The hexoses have five hydroxyl-groups, since, when heated with acetic anhydride and a small quantity of sodium acetate or zinc chloride, they yield penta-acetyl-derivatives.

These facts indicate the existence in an aldohexose of

a normal carbon chain, C—C—C—C—C—C;

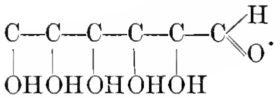
an aldehydo-group,



$$\mathrm{C{-}C{-}C{-}C{-}C{-}C}\Big\langle^{\mathrm{H}}_{\mathrm{O}};$$

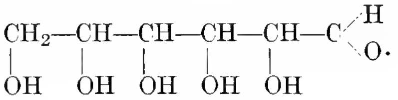
and

five hydroxyl-groups,



$$\begin{array}{cccccc} \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}\Big\langle^{\mathrm{H}}_{\mathrm{O}}. \\ | & | & | & | & | & \\ \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \end{array}$$

There are six other hydrogen atoms in the formula $C_6H_{12}O_6$, and these will fit in with the last scheme, if the C-atoms of the chain are singly linked to each other: the formula of an aldohexose will then be

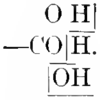


$$\begin{array}{cccccc} \mathrm{CH_2}- & \mathrm{CH}- & \mathrm{CH}- & \mathrm{CH}- & \mathrm{CH}- & \mathrm{C}\Big\langle^{\mathrm{H}}_{\mathrm{O}}. \\ | & | & | & | & | & \\ \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \end{array}$$

In these formulæ a somewhat arbitrary assumption has been made as to the distribution of the hydroxyl-groups and hydrogen atoms relative to the carbon atoms; it is, however, in accordance with the principle (155) that a carbon atom cannot usually have linked to it more than one hydroxyl-group. A more convincing proof of the fact that the monoses do not contain two hydroxyl-groups attached to the same carbon atom, is afforded by the following considerations.

When a hexose, $C_6H_{12}O_6$, is reduced to a hexahydric alcohol, $C_6H_{14}O_6$, only two hydrogen atoms are added, and this addition must take place at the doubly-linked oxygen atom, since the carbon chain remains unbroken. If the hexose contains two hydroxyl-groups attached to one carbon atom, so must also the hexahydric alcohol derived from it. Compounds containing a C-atom linked to two OH-groups readily lose water, with formation of aldehydes or ketones: they also possess most of the properties characteristic of these substances (201). The hexahydric alcohols, however, have an exclusively alcoholic character, and do not exhibit any of the reactions of aldehydes and ketones. It follows that the hexahydric alcohols, and hence the hexoses, cannot contain two hydroxyl-groups linked to a single carbon atom.

The possibility of the attachment of three hydroxyl-groups to one carbon atom is also excluded, since, when the production of a compound with such a grouping might be expected, water is always eliminated, with formation of an acid (86):



$$\begin{array}{r@{}l} & \mathrm{O\ H|} \\ -\mathrm{C} & \mathrm{O|\overline{H}.} \\ & \underline{\mathrm{|\overline{OH}}} \end{array}$$

The monoses have none of the properties which distinguish acids: their aqueous solutions do not conduct the electric current; whereas the dissociation-constant for an acid containing so many OH-groups should be considerably higher than for a saturated fatty acid, such as acetic acid (183).

> With calcium and strontium hydroxides, and other bases, the carbohydrates form compounds called *saccharates*, which are, therefore, to be looked upon as alkoxides (55).

It follows from these considerations that the constitution of the aldohexoses cannot be other than that given above, and, since the same method of proof is applicable to each member, they must all have the same constitutional formula, and are therefore stereoisomerides. This is due to the presence in the molecule of asymmetric carbon atoms: an aldohexose has four such atoms, indicated by asterisks in the formula

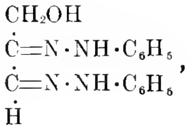
$$CH_2OH\cdot\overset{*}{C}HOH\cdot\overset{*}{C}HOH\cdot\overset{*}{C}HOH\cdot\overset{*}{C}HOH\cdot C\genfrac{}{}{0pt}{}{H}{O}.$$

Methods of Formation of the Monoses.

207. 1. From the polyoses, by hydrolysis; that is, decomposition with addition of water

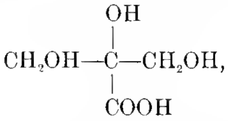
2. From the corresponding alcohols, by the action of oxidizing agents, such as nitric acid. Arabitol, $C_5H_{12}O_5$, yields arabinose, $C_5H_{10}O_5$; xylitol yields xylose; mannitol yields mannose; etc.

When glycerol is carefully oxidized with nitric acid, or with bromine and sodium hydroxide, a syrupy liquid is obtained, which shows the four reactions typical of monoses (205): it is called *glycerose*. Its osazone, *glycerosazone*,



$$\begin{array}{l} CH_2OH \\ \dot{C}{=}N\cdot NH\cdot C_6H_5 \\ \dot{C}{=}N\cdot NH\cdot C_6H_5 \\ \dot{H} \end{array},$$

crystallizes in yellow leaves, melting at 131°. Glycerose is *dihydroxyacetone*, $CH_2OH\cdot CO\cdot CH_2OH$, as is proved by the cyanohydrin-synthesis (182, 5), by means of which trihydroxy*iso*butyric acid,



$$\begin{array}{ccc} & OH & \\ & | & \\ CH_2OH— & C & —CH_2OH, \\ & | & \\ & COOH & \end{array}$$

is obtained. The structure of this acid is inferred from its reduction to *iso*butyric acid. In accordance with the nomenclature already indicated, glycerose is a *triose*.

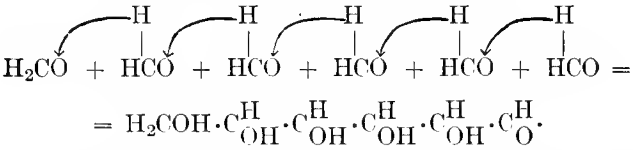
When sorbose-bacteria are cultivated in a solution of glycerol, the final product obtained by the action of the atmospheric oxygen is dihydroxyacetone. These bacteria can also oxidize other polyhydric alcohols to ketoses.

3. From bromo-compounds of aldehydes, by exchange of bromine for hydroxyl, which can be effected by cold baryta-water.

In this manner the simplest member of the sugars, *glycollaldehyde*, $CH_2OH\cdot C\genfrac{}{}{0pt}{}{H}{O}$, is obtained from monobromoaldehyde, $CH_2Br\cdot C\genfrac{}{}{0pt}{}{H}{O}$: it shows all the reactions of the monoses.

The addition of bromine to acroleïn (147) yields $CH_2Br \cdot CHBr \cdot C^{H}_{O}$, which is converted by the action of baryta-water into glyceraldehyde.

4. From formaldehyde, by the action of lime-water (aldol-condensation). The crude condensation-product, called *formose,* is a sweet, syrup-like substance: it consists of a mixture of compounds of the formula $C_6H_{12}O_6$. In this reaction, six molecules of formaldehyde undergo the aldol-condensation (115):



$$H_2CO + \overset{H}{HCO} + \overset{H}{HCO} + \overset{H}{HCO} + \overset{H}{HCO} + \overset{H}{HCO} =$$

$$= H_2COH \cdot C^{H}_{OH} \cdot C^{H}_{OH} \cdot C^{H}_{OH} \cdot C^{H}_{OH} \cdot C^{H}_{O}.$$

By the aid of sunlight and moisture, plants are able to convert the carbon dioxide of the atmosphere into starch, a polyose of the formula $(C_6H_{10}O_5)_x$. The reaction may be represented empirically, thus:

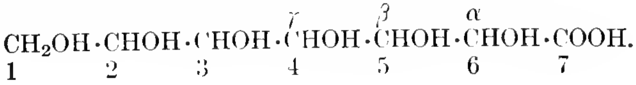
$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2.$$

Von Baeyer has suggested that the carbon dioxide, CO_2, is first reduced to formaldehyde, CH_2O, which condenses to a monose, the latter being then converted into the polyose, starch.

Berthelot has obtained substances of the nature of carbohydrates by the action of a silent electric discharge on a mixture of carbon dioxide, carbon monoxide, and hydrogen.

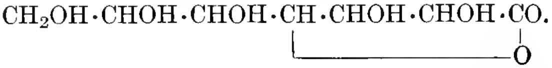
A hexose can also be obtained from glyceraldehyde, two molecules of which yield, by the aldol-condensation, one molecule of the hexose. This hexose is called *acrose,* on account of its relation to acroleïn, from which glyceraldehyde can be obtained by method 3. Acrose is a constituent of formose, and, like all compounds prepared by purely chemical synthesis, is optically inactive.

5. A very important general method for the conversion of an aldose into another containing one more carbon atom in the molecule is the formation of an addition-product with hydrocyanic acid. An aldohexose yields a cyanohydrin which is converted on hydrolysis into a monobasic acid containing seven C-atoms,



$$\underset{1}{CH_2OH} \cdot \underset{2}{CHOH} \cdot \underset{3}{CHOH} \cdot \underset{4}{\overset{\gamma}{CHOH}} \cdot \underset{5}{\overset{\beta}{CHOH}} \cdot \underset{6}{\overset{\alpha}{CHOH}} \cdot \underset{7}{COOH}.$$

The γ-hydroxyl-group reacts easily with the carboxyl-group, forming a lactone,



$$\mathrm{CH_2OH\cdot CHOH\cdot CHOH\cdot \underbrace{CH\cdot CHOH\cdot CHOH\cdot CO}_{O}.}$$

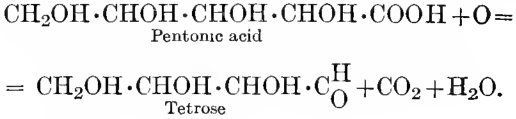
In aqueous solution, these lactones can be reduced by sodium-amalgam to the corresponding aldehydes, the aldoses.

The great importance of this synthesis consists in the theoretical possibility of obtaining from the lower members, step by step, aldoses with any desired number of C-atoms in the molecule, by repeated application of the cyanohydrin-synthesis, and reduction of the lactone thus obtained. It has thus been possible to prepare *nonoses*, with nine C-atoms, by conversion of an aldohexose into a *heptonic acid*, the lactone of which can then be reduced to a *heptose*. This compound can be converted into an *octose*, and the latter into a nonose, by the same process.

I. MONOSES.

Pentoses.

208. Reference has already been made to the dioses and trioses (204). Tetroses can be obtained by the oxidation of pentonic acid, in the form of its calcium salt, by means of hydrogen peroxide, a small quantity of ferric acetate being used as a catalyst:



$$\underset{\text{Pentonic acid}}{\mathrm{CH_2OH\cdot CHOH\cdot CHOH\cdot CHOH\cdot COOH}}+\mathrm{O}=$$

$$=\underset{\text{Tetrose}}{\mathrm{CH_2OH\cdot CHOH\cdot CHOH\cdot C}}{}^{\mathrm{H}}_{\mathrm{O}}+\mathrm{CO_2}+\mathrm{H_2O}.$$

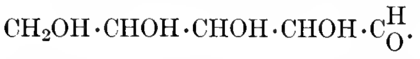
Also pentoses can be obtained from hexoses by this method.

A number of different pentoses have been identified, among them *arabinose* and *xylose*, both of which are present in many plants as polyoses, called *pentosans*.

Arabinose can be prepared by boiling gum-arabic or cherry-gum with dilute acids. *Xylose*, or *wood-sugar*, can be got similarly from bran, wood, straw, and other substances, especially the shells of apricot-stones. Arabinose and xylose can be prepared from any plant-cells which have been converted into wood, and which show the reactions of lignin (227). The racemic modification of arabinose is present in the urine of patients suffering from the disease known as *pentosuria.*

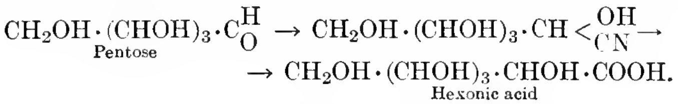
Arabinose forms well-defined crystals, melts at 160°, and has a sweet taste. Its osazone melts at 157°. Xylose also crystallizes well, and yields an osazone which melts at 160°.

Arabinose and xylose are aldoses, and have the same formula,



$$CH_2OH\cdot CHOH\cdot CHOH\cdot CHOH\cdot C^{H}_{O}.$$

This constitution is proved by their conversion, on gentle oxidation with bromine-water, into *arabonic acid* and *xylonic acid* respectively, both of which have the formula $CH_2OH\cdot(CHOH)_3\cdot COOH$, and are therefore stereoisomeric. On stronger oxidation, both arabinose and xylose yield *trihydroxyglutaric acid,* $COOH\cdot(CHOH)_3\cdot COOH$, the constitution of which follows from its reduction to glutaric acid. The acid obtained from arabinose is optically active, and that from xylose is inactive, so that they, too, are stereoisomerides. On reduction, these two pentoses yield respectively *arabitol* and *xylitol,* which are stereoisomeric pentahydric alcohols. Arabinose and xylose can be converted into hexoses by the cyanohydrin-synthesis, a proof that neither contains a C-atom in union with more than one OH-group (206), and that each has a normal carbon chain:



$$\underset{\text{Pentose}}{CH_2OH\cdot(CHOH)_3\cdot C^{H}_{O}} \rightarrow CH_2OH\cdot(CHOH)_3\cdot CH<^{OH}_{CN} \rightarrow$$
$$\rightarrow \underset{\text{Hexonic acid}}{CH_2OH\cdot(CHOH)_3\cdot CHOH\cdot COOH}.$$

This hexonic acid yields a lactone which, on reduction, gives the hexose. Arabinose and xylose contain three asymmetric C-atoms, and are optically active.

The pentoses have one property in common, by which they may be recognized and distinguished from hexoses. When boiled with dilute sulphuric acid, or hydrochloric acid of sp. gr. 1·06, the pentoses and their polyoses form a volatile compound, *furfuraldehyde,* $C_5H_4O_2$ (458), which, on treatment with aniline and hydrochloric acid, yields an intense red dye.

The presence of the polyose of xylose can be detected in such a substance as straw by distillation with hydrochloric acid of sp. gr.

1·06. With aniline and hydrochloric acid, the distillate gives an intense red coloration, and with phenylhydrazine yields a phenylhydrazone very sparingly soluble in water. Both these reactions indicate the presence of furfuraldehyde.

Hexoses.

209. The *hexoses* are colourless compounds of sweet taste, which are difficult to crystallize, and cannot be distilled without decomposition. They dissolve readily in water, with difficulty in absolute alcohol, and are insoluble in ether. Since all the aldohexoses are stereoisomerides (**206**), their oxidation-products, the monobasic and dibasic acids, are also stereoisomerides.

1. *Dextrose* (d-*glucose* or *grape-sugar*) is present in many plants, notably in the juice of grapes, and in other sweet fruits: it is found in the urine of diabetic patients, and in small quantities in normal urine. It can be obtained from many polyoses; for example, cane-sugar is converted by hydrolysis—*inversion* (**215**)—into a mixture of dextrose and lævulose (**209**, 2), called *invert-sugar*. The technical preparation of dextrose from starch, by boiling with dilute acids, is likewise a case of hydrolysis.

Dextrose crystallizes from water, or alcohol, with some difficulty: the crystals obtained from methyl alcohol contain no water of crystallization, and melt at 146°. It is mentioned in **47** that dextrose can be readily fermented, producing chiefly alcohol and carbon dioxide. Natural dextrose is dextro-rotatory: a lævo-rotatory and an optically inactive modification have been artificially prepared. The dextro-rotatory, lævo-rotatory, and optically inactive isomerides are respectively distinguished by the prefixes *d* (*dexter*), *l* (*lævus*), and *i* (*inactive*); thus, *d*-glucose, *l*-glucose, *i*-glucose.

By convention, all other monoses derived from a *d*-hexose, *l*-hexose, or *i*-hexose are also distinguished by the letters *d*, *l*, or *i*, even when they possess a rotatory power opposite in sign to that indicated by these letters. Thus, lævulose or ordinary fructose, which can be obtained from dextrose or *d*-glucose, and is lævo-rotatory, is also called *d*-fructose on account of its genetic relation to *d*-glucose. The same method of classification is adopted for the hexahydric alcohols, the hexonic acids, and in general for all derivatives of the hexoses.

Dextrose is an aldose, as is proved by its oxidation to a hexonic acid, d-*gluconic acid*, $CH_2OH \cdot (CHOH)_4 \cdot COOH$: further oxidation produces the dibasic *d*-saccharic acid,

$$COOH \cdot (CHOH)_4 \cdot COOH.$$

Saccharic acid forms a characteristic potassium hydrogen salt of slight solubility, which serves as a test for dextrose. The substance suspected of containing dextrose is oxidized with nitric acid: saccharic acid is produced from this hexose, if present, and can be precipitated as potassium hydrogen salt by addition of a concentrated solution of potassium acetate.

On reduction, dextrose yields a hexahydric alcohol, d-*sorbitol*: it also gives an osazone, d-*glucosazone*, which is soluble with difficulty in water, and crystallizes in yellow needles which melt at 204°–205°

Solutions of dextrose and many other sugars furnish examples of a phenomenon called *mutarotation*. When freshly dissolved, such substances have a rotatory power other than that possessed by them after the lapse of a comparatively short interval of time. Thus, an aqueous solution of dextrose at first produces a rotation $[\alpha]_D = 110°$: after some hours it produces a constant rotation $[\alpha]_D = 52 \cdot 5°$ The attainment of a constant rotatory power is much hastened by boiling the solution, and is effected at once by addition of a small quantity of caustic potash or ammonia.

The explanation of this phenomenon must be sought in the partial conversion of the dextrose or other sugar into another modification of different rotatory power. When the rotation has become constant, there is equilibrium between the two modifications.

Tanret has prepared three different crystalline modifications of dextrose, denoted by α, β, and ε. Ordinary dextrose is the α-modification: it crystallizes with one molecule of water. When dissolved quickly in cold water, the solution produces a rotation $[\alpha]_D = 110°$. When the solid α-form is heated for some days at 105°, it is changed to the β-form. In aqueous solution the β-modification at first only rotates the plane through $[\alpha]_D = 19°$: when allowed to remain for some time, or boiled, or mixed with a trace of alkali, the rotation rises to $[\alpha]_D = 52 \cdot 5°$. When dissolved in water, the ε-modification at once causes a rotation $[\alpha]_D = 52 \cdot 5°$, indicating that it is not an independent form, but a mixture in equilibrium of the α-modification and β-modification.

Tanret has proved by experiment that this surmise is correct. A very concentrated solution of the ε-modification was made, and crystallized at 0°. When a solution of the crystals thus obtained was prepared at a low temperature, its rotation was diminished by addition of a small quantity of ammonia, proving that the crystals belonged to the α-modification. If the ε-form is a mixture of the α-modification and the β-modification, the latter must have remained in solution in the mother-liquor, and addition of alkali should increase the rotation of this residual solution. Experiment proved that this was so.

Opinion is divided regarding the formula to be assigned to the α-modification and β-modification respectively, but both are known to have the same molecular weight. Some chemists think that one has the formula $\mathrm{CH_2OH \cdot (CHOH)_4 \cdot C^{H}_{O}}$, containing the aldehydo-group, $\mathrm{—C^{H}_{O}}$, and that the other has a lactone-formula. Others consider it probable that both modifications have the lactone-constitution, and are stereoisomeric.

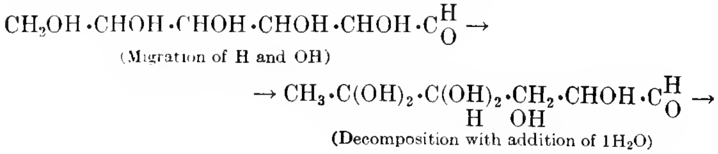
With a small quantity of water, dextrose yields a colourless syrup used in the preparation of liqueurs and of confectionery.

The *mechanism of the formation of ethyl alcohol and carbon dioxide by the fermentation of dextrose* is probably best explained by assuming alterations in the relative positions occupied by the hydroxyl-groups and hydrogen atoms. It may be supposed that elimination of water in the usual manner first takes place, being followed by the migration of one hydrogen atom. These changes involve the transformation of the group $\mathrm{—CHOH \cdot CHOH—}$ by abstraction of water into $\mathrm{—CH{=}C(OH)—}$, which then changes to $\mathrm{—CH_2 \cdot CO—}$. The result is the same as that produced by an exchange of position between hydrogen and hydroxyl, followed by elimination of water:

$$\mathrm{—CHOH \cdot CHOH— \rightarrow —CH_2 \cdot C(OH)_2— \rightarrow —CH_2 \cdot CO—}.$$

Analogous phenomena are known, among them the formation of acroleïn from glycerol (158), of pyroacemic from tartaric acid (250), and of oxalacetic acid, $\mathrm{COOH \cdot CO \cdot CH_2 \cdot COOH}$, from tartaric acid.

Methylglyoxal, which was isolated as osazone, is an intermediate decomposition-product in the interaction of dextrose and dilute alkalis, as indicated in the following scheme:

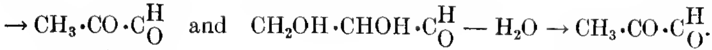


$$\mathrm{CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHOH \cdot C^{H}_{O}} \rightarrow$$

(Migration of H and OH)

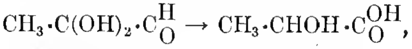
$$\rightarrow \mathrm{CH_3 \cdot C(OH)_2 \cdot \underset{H}{C(OH)_2} \cdot \underset{OH}{CH_2} \cdot CHOH \cdot C^{H}_{O}} \rightarrow$$

(Decomposition with addition of $1\mathrm{H_2O}$)



$$\rightarrow \underset{\text{Methylglyoxal}}{CH_3\cdot CO\cdot C_{O}^{H}} \quad \text{and} \quad CH_2OH\cdot CHOH\cdot C_{O}^{H} - H_2O \rightarrow \underset{\text{Methylglyoxal}}{CH_3\cdot CO\cdot C_{O}^{H}}.$$

Lactic acid has been identified as an intermediate product in alcoholic fermentation, and may be regarded as derived from methylglyoxal in accordance with the scheme



$$\underset{\text{Methylglyoxal}}{CH_3\cdot C(OH)_2\cdot C_{O}^{H}} \rightarrow \underset{\text{Lactic acid}}{CH_3\cdot CHOH\cdot C_{O}^{OH}},$$

resulting from a change of position between hydroxyl and hydrogen. The lactic acid then loses carbon dioxide, yielding ethyl alcohol:

$$CH_3\cdot CHOH\cdot CO_2H = CH_3\cdot CH_2OH + CO_2.$$

It is not improbable that two enzymes play a part in these reactions. One of them may occasion the interchange of position leading to the formation of lactic acid; the other may effect the decomposition of the lactic acid into alcohol and carbon dioxide.

The conversion of dextrose into butyric acid by the butyric fermentation can also be explained by assuming the intermediate formation of lactic acid, and its subsequent transformation into formic acid and acetaldehyde. Condensation of acetaldehyde produces aldol, which yields butyric acid by transposition of H and OH:

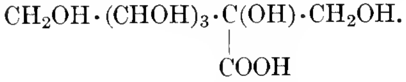
$$CH_3\cdot CHO + CH_3\cdot CHO = \underset{\text{Aldol}}{CH_3\cdot CHOH\cdot CH_2\cdot CHO} \rightarrow \underset{\text{Butyric acid}}{CH_3\cdot CH_2\cdot CH_2\cdot COOH}.$$

2. *Lævulose* (d-*fructose* or *fruit-sugar*) is present along with dextrose in most sweet fruits. It is a constituent of invert-sugar (**217**), and of honey, which is chiefly a natural invert-sugar. When hydrolyzed, *inulin*, a polyose contained in dahlia-tubers, yields only lævulose, just as starch yields dextrose. Lævulose crystallizes with difficulty, being readily soluble in water, although less so than dextrose. It is lævo-rotatory, and can be fermented.

Lævulose is a type of the ketoses, but few of which are known. Its formula, $CH_2OH\cdot(CHOH)_3\cdot CO\cdot CH_2OH$, is inferred from the following considerations. First, when oxidized with mercuric oxide in presence of baryta-water, it is converted into glycollic acid, $CH_2OH\cdot COOH$, and trihydroxyglutaric acid,

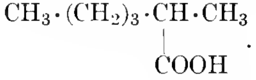
$$COOH\cdot(CHOH)_3\cdot COOH.$$

Since oxidation takes place in the carbonyl-group, the production of these acids necessitates the adoption of this constitutional formula. Second, application of the cyanohydrin-synthesis to a compound of this constitution would yield a heptonic acid with the formula



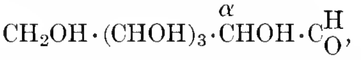
$$CH_2OH\cdot(CHOH)_3\cdot\underset{\displaystyle COOH}{\underset{|}{C}}(OH)\cdot CH_2OH.$$

That the heptonic acid obtained from lævulose has this constitution, is proved by heating it at a high temperature with hydriodic acid, whereby all the hydroxyl-groups are replaced by hydrogen, and a heptylic acid is formed. This acid is identical with the synthetic *methyl-*n*-butylacetic acid* (**251**, 2),



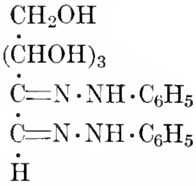
$$CH_3\cdot(CH_2)_3\cdot\underset{\displaystyle COOH}{\underset{|}{C}}H\cdot CH_3.$$

The osazone of lævulose is identical with that of dextrose. A comparison of the formula of dextrose,



$$CH_2OH\cdot(CHOH)_3\cdot\overset{\alpha}{C}HOH\cdot C{}^{H}_{O},$$

with that of lævulose, $CH_2OH\cdot(CHOH)_3\cdot CO\cdot CH_2OH$, shows that the two osazones can only be identical if the α-C-atom of dextrose, and the terminal C-atom of lævulose, respectively unite, after formation of the hydrazone, with the second phenylhydrazine-residue: that is, when in both cases this reaction takes place at a C-atom directly linked to a carbonyl-group. For this reason, it is assumed that the formation of an osazone always results in the union of two phenylhydrazine-residues with neighbouring C-atoms. d-*Glucosazone*, or d-*fructosazone*, has therefore the constitution



$$\begin{array}{l} CH_2OH \\ \dot{(}CHOH)_3 \\ \dot{C}{=}N\cdot NH\cdot C_6H_5 \\ \dot{C}{=}N\cdot NH\cdot C_6H_5 \\ \dot{H} \end{array}$$

When osazones are carefully warmed with hydrochloric acid, two molecules of phenylhydrazine are eliminated, with formation of compounds, *osones*, containing two carbonyl-groups. For example, *d*-glucosazone yields d-*glucosone*,

$$CH_2OH\cdot(CHOH)_3\cdot CO\cdot C{}^{H}_{O}.$$

The osones can be reduced by treatment with zinc-dust and acetic acid, and it is found that addition of hydrogen always takes place at the terminal C-atom. *d*-Glucosone yields lævulose,

$$CH_2OH\cdot(CHOH)_3\cdot CO\cdot CH_2OH.$$

The reaction affords a means of converting aldoses into ketoses:

Aldose → Osazone → Osone → Ketose.

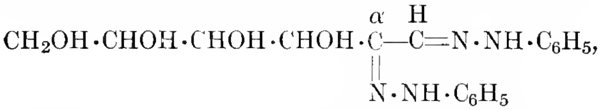
Inversely, an aldose can be obtained from a ketose. On reduction, the latter yields a hexahydric alcohol, which is converted by oxidation into a monobasic hexonic acid. This substance loses water, yielding the corresponding lactone, which on reduction gives the aldose:

Ketose → Hexahydric Alcohol → Hexonic Acid → Lactone → Aldose.

3. d-*Mannose* is an aldose, and is present as a polyose in the vegetable-ivory nut: it is also obtained by the careful oxidation of the hexahydric alcohol *mannitol*, found in several plants. *d*-Mannose, a hard, amorphous, hygroscopic substance, can be readily fermented, and is very soluble in water. It yields a characteristic hydrazone which melts at 195°–200°, and, unlike the hydrazones of the other monoses, dissolves with difficulty in water. On oxidation, *d*-mannose is first converted into the monobasic d-*mannonic acid*, $CH_2OH\cdot(CHOH)_4\cdot COOH$, and then into the dibasic d-*manno-saccharic acid*, $COOH\cdot(CHOH)_4\cdot COOH$. It yields dextrose by a method generally applicable to the conversion of aldoses into their stereoisomerides. For this purpose, it is first converted into *d*-mannonic acid. On boiling the solution of this substance in quinoline (463), it is partly transformed into the stereoisomeric *d*-gluconic acid, the lactone of which can be reduced to dextrose. Inversely, *d*-gluconic acid is partly changed into *d*-mannonic acid, by boiling its quinoline solution, so that dextrose can thus be converted into *d*-mannose.

Mannonic acid is one of the intermediate products in Emil Fischer's synthesis of dextrose. He converted glyceraldehyde into acrose (207, 4), and this into *i*-mannitol, by reduction with sodium-amalgam. On oxidation, *i*-mannitol yields first *i*-mannose, and then *i*-mannonic acid, which can be resolved, by means of its strychnine salt, into its optically active modifications. When the *d*-mannonic acid thus obtained is heated with pyridine, it is converted into *d*-gluconic acid, the lactone of which, on reduction with sodium-amalgam, yields dextrose.

The stereoisomerism of *d*-mannose and dextrose, as well as of *d*-mannonic acid and *d*-gluconic acid, is occasioned only by different grouping round the α-C-atom, since the osazone of *d*-mannose is identical with that of dextrose. As this has the constitution



$$CH_2OH\cdot CHOH\cdot CHOH\cdot CHOH\cdot\underset{\underset{\displaystyle N\cdot NH\cdot C_6H_5}{\|}}{\overset{\alpha}{C}}-\overset{H}{C}=N\cdot NH\cdot C_6H_5,$$

these osazones can only be identical when the residue

$$CH_2OH\cdot(CHOH)_2\cdot CHOH-$$

in *d*-mannose and dextrose is also identical: their stereoisomerism can then only result from a difference in the arrangement of the groups linked to the α-C-atom.

So far as the transformations of the monobasic hexonic acids when boiled with quinoline or pyridine have been studied, it has always been found that the alteration takes place, as in the above instance, at only one C-atom, and this the one adjoining the aldehydo-group, the α-C-atom.

Very remarkable is the conversion into each other, discovered by Lobry de Bruyn, of dextrose, lævulose, and mannose, under the influence of very dilute alkalis. Their rotatory power is considerably reduced thereby: each of these hexoses forms both the others, and the one originally present is not completely converted. An equilibrium is thus established which may be represented by the scheme

$$\text{Dextrose} \rightleftarrows \text{Lævulose} \rightleftarrows \text{Mannose}.$$

That lævulose is actually an intermediate product of this transformation, is shown by the behaviour of the dextro-rotatory solution of mannose, which, owing to the formation of lævulose, first develops lævo-rotation, which gradually decreases as the dextro-rotatory dextrose is produced.

4. d-*Galactose* can be obtained by the hydrolysis of lactose, or by the oxidation of the hexahydric alcohol *dulcitol,* which occurs in certain plants. *d*-Galactose is crystalline, melting at 168°; it is strongly dextro-rotatory, is capable of undergoing fermentation, and exhibits mutarotation. Galactose is proved to be an aldose by its conversion, on oxidation, into the monobasic d-*galactonic acid*, $C_6H_{12}O_7$. Further oxidation yields the sparingly soluble dibasic *mucic acid*, $COOH \cdot (CHOH)_4 \cdot COOH$, which is optically inactive, and cannot be resolved into optically active components: its formation serves as a test for *d*-galactose. This is carried out by oxidizing the hexose under examination with nitric acid.

Their conversion into *lævulic acid* (**252**), on treatment with hydrochloric acid, constitutes a general reaction for the hexoses. Brown, amorphous masses, known as *humic substances,* are produced at the same time. Lævulic acid can be identified by means of its silver salt, which dissolves with difficulty, and yields characteristic crystals.

The identification of the constituents of a mixture of monoses can often be readily effected by the aid of phenylhydrazine and its substitution-products (**344**), the tendency of each monose to form a phenylhydrazone or osazone depending on the particular hydrazine-derivative employed. Thus, from a solution containing arabinose and dextrose unsymmetrical methylphenylhydrazine, $C_6H_5N(CH_3) \cdot NH_2$, dissolved in acetic acid precipitates arabinose-methylphenylhydrazone. If this is filtered off and the liquid warmed after addition of an acetic-acid solution of phenylhydrazine, phenylglucososazone crystallizes out.

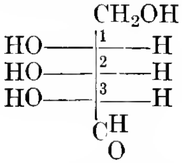
Heptoses, Octoses, and Nonoses.

210. These substances are not natural products, but can be built up from the hexoses by the cyanohydrin-synthesis: for example, mannose yields *mannoheptose*, *manno-octose*, and *mannononose.*

Stereochemistry of the Monoses.

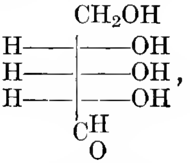
211. It was stated (206) that all the aldohexoses and aldopentoses have the same structure, and that, in consequence, their isomerism must be stereoisomerism. Although it would be beyond the scope of this book to deduce the configuration of all the pentoses and hexoses mentioned here, it is desirable to indicate how this is determined for such compounds; that is, for those containing several asymmetric carbon atoms in the molecule.

It was mentioned (191) that the presence of two dissimilar asymmetric C-atoms in a molecule causes the existence of a greater number of stereoisomerides than that of two similar asymmetric C-atoms. It will be seen from a projection-formula that the principle applies to a greater number of asymmetric C-atoms in the molecule. The projection-formulæ for two aldopentoses,



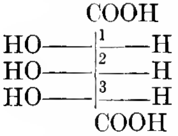
$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{HO}- & |^{1} & -\mathrm{H} \\ \mathrm{HO}- & |^{2} & -\mathrm{H} \\ \mathrm{HO}- & |^{3} & -\mathrm{H} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

and



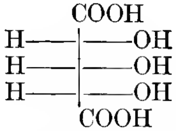
$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH}, \\ \mathrm{H}- & | & -\mathrm{OH} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

cannot be made to coincide by rotation in the plane of the paper (191): the aldopentoses, therefore, are not identical. The corresponding trihydroxyglutaric acids



$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{HO}- & |^{1} & -\mathrm{H} \\ \mathrm{HO}- & |^{2} & -\mathrm{H} \\ \mathrm{HO}- & |^{3} & -\mathrm{H} \\ & \mathrm{COOH} & \end{array}$$

and



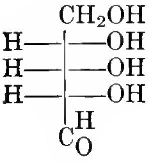
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

are, however, identical, since their projection-formulæ can be made to coincide. In these compounds the asymmetric C-atoms 1 and 3 are similar, while in the pentoses they are dissimilar.

Assuming that the determination of the configuration of a trihydroxyglutaric acid is possible, and that it leads to the projection-formula given above, it follows that the pentose from which this acid is obtained by oxidation must have one of the above configurations, and that all others are excluded. It thus only remains to distinguish between these two configurations.

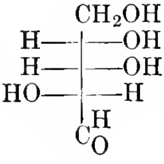
In order to determine the stereochemical structure of a pentose, it is, therefore, first necessary to determine that of the corresponding trihydroxyglutaric acid. The optical behaviour of these acids affords a means of determining their stereochemical structure. Xylose, which is optically active, is converted by oxidation into an optically inactive trihydroxyglutaric acid which melts at 152°. Since an optically inactive substance is here obtained from an optically active one, not from a racemic compound, the inactivity must be due to intramolecular compensation, a fact which must find expression in the configuration allotted to this particular trihydroxyglutaric acid. The projection-formula of a compound which is optically inactive on account of intramolecular compensation must fulfil this condition: itself and its mirror-image must be capable of being made to coincide by rotation in the plane of the paper; that is, itself and its mirror-image must be identical. For, if it were otherwise, two enantiomorphous configurations—the formula and its mirror-image—would be possible, while for intramolecular compensation only one configuration is possible.

The above reasoning may be applied to the determination of the stereochemical structure of arabinose. Eight stereoisomeric formulæ are possible for a pentose, but, by arranging these in pairs of mirror-images, and taking one of each pair, four different types are obtained:



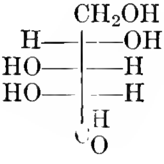
$$\begin{array}{rcl} & CH_2OH & \\ H- & | & -OH \\ H- & | & -OH \\ H- & | & -OH \\ & C{}^{H}_{O} & \end{array}$$

I.



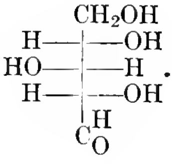
$$\begin{array}{rcl} & CH_2OH & \\ H- & | & -OH \\ H- & | & -OH \\ HO- & | & -H \\ & C{}^{H}_{O} & \end{array}$$

II.



$$\begin{array}{rcl} & CH_2OH & \\ H- & | & -OH \\ HO- & | & -H \\ HO- & | & -H \\ & C{}^{H}_{O} & \end{array}$$

III.



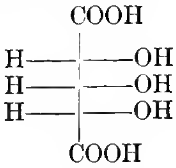
$$\begin{array}{rcl} & CH_2OH & \\ H- & | & -OH \\ HO- & | & -H \\ H- & | & -OH \\ & C{}^{H}_{O} & \end{array}.$$

IV.

The mirror-image of I. is represented on p. 272.

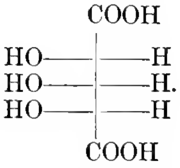
Arabinose is converted by oxidation into an optically active trihydroxyglutaric acid. This excludes the trihydroxyglutaric acids which could be obtained from types I. and IV., since each of these could be made to coincide with its mirror-image, and thus would be optically inactive:

I.



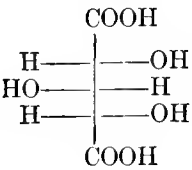
$$\begin{array}{rcl} & COOH & \\ H- & | & -OH \\ H- & | & -OH \\ H- & | & -OH \\ & COOH & \end{array}$$

identical with its mirror-image,



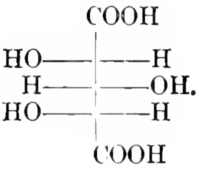
$$\begin{array}{rcl} & COOH & \\ HO- & | & -H \\ HO- & | & -H. \\ HO- & | & -H \\ & COOH & \end{array}$$

IV.



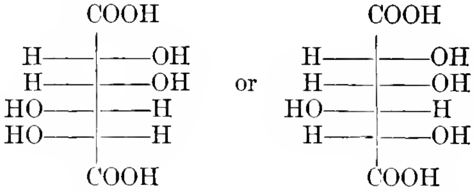
$$\begin{array}{rcl} & COOH & \\ H- & | & -OH \\ HO- & | & -H \\ H- & | & -OH \\ & COOH & \end{array}$$

identical with its mirror-image,



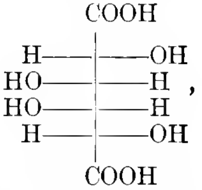
$$\begin{array}{rcl} & COOH & \\ HO- & | & -H \\ H- & | & -OH. \\ HO- & | & -H \\ & COOH & \end{array}$$

The fact that by the aid of the cyanohydrin-synthesis arabinose can be converted into a mixture of dextrose and mannose, which on oxidation yields the optically active saccharic acid and mannosaccharic acid, enables a choice between types II. and III. to be made. Since in the cyanohydrin-synthesis only the group C_{O}^{H} in $CHOH \cdot C_{O}^{H}$ is altered, the configuration of the rest of the C-atoms remaining unchanged, saccharic acid and mannosaccharic acid must have the stereochemical structure



$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{HO}- & | & -\mathrm{H} \\ \mathrm{HO}- & | & -\mathrm{H} \\ & \mathrm{COOH} & \end{array} \quad \text{or} \quad \begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{HO}- & | & -\mathrm{H} \\ \mathrm{H}- & | & -\mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

if arabinose is represented by formula II. Neither of these can be made to coincide with its mirror-image, so that formula II. is assumed to represent arabinose. Formula III. is excluded, since otherwise one of the acids mentioned above must have the stereochemical constitution



$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{HO}- & | & -\mathrm{H} \\ \mathrm{HO}- & | & -\mathrm{H} \\ \mathrm{H}- & | & -\mathrm{OH} \\ & \mathrm{COOH} & \end{array},$$

which is identical with its mirror-image: one of the acids would then be optically inactive, which is not the case.

Arabinose has, therefore, a formula of the type II., but it is still uncertain whether it should be represented by the formula given above, or by its mirror-image.

II. DIOSES.

212. Numerous *dioses* (or *bioses*) are known, which are almost exclusively derived from hexoses, and therefore have the formula

$$C_{12}H_{22}O_{11} = 2C_6H_{12}O_6 - H_2O.$$

No dioses are known which can be decomposed into a pentose and a hexose: on hydrolysis, some of the hexodioses yield two different monoses, and some only one.

The hydrolysis can be effected not only by boiling with dilute acids, but also by the action of enzymes (**219**.) On account of the readiness with which decomposition with water takes place, it is assumed that the monoses from which a diose is formed are not linked together through the carbon atoms, but through one or more oxygen atoms.

Hitherto, all attempts to synthesize natural dioses have failed.

EMIL FISCHER has, however, isolated a diose, iso*lactose*, from a mixture of dextrose and galactose: this was treated with an enzyme called *lactase*, present in kephir-granules.

FISCHER has also prepared artificial dioses synthetically from monoses, such as dextrose. On treatment with acetyl chloride, these substances yield acetochloro-compounds with four acetyl-groups, the fifth hydroxyl-group of the monose being replaced by a Cl-atom. The formula of these acetochloro-compounds is $C_6H_7OCl(OC_2H_3O)_4$. They are converted by a monose and sodium alkoxide into tetra-acetyl-derivatives of dioses, from which the acetyl-groups can be eliminated by means of sodium hydroxide, and the free dioses then isolated as osazones. Dextrose converts aceto-chlorogalactose into a diose probably identical with melediose (**221**).

Maltose.

213. *Maltose* in the crystallized state has the formula $C_{12}H_{22}O_{11} + H_2O$, and can be prepared from starch by the action of diastase (**47**). It is an important intermediate product in the industrial production of alcohol.

Maltose crystallizes in small, white needles, and is strongly dextro-rotatory. When boiled with dilute mineral acids, it yields only dextrose. It exhibits all the characteristics of the monoses: thus, it reduces an alkaline copper solution; yields an osazone, *maltosazone* ($C_{12}H_{22}O_{11} - 2H_2O - 2H + 2C_6H_5NH \cdot NH_2$); and it can be oxidized to the monobasic *maltobionic acid*, $C_{12}H_{22}O_{12}$, which, on hydrolysis, splits up into dextrose and *d*-gluconic acid, $CH_2OH \cdot (CHOH)_4 \cdot COOH$.

These properties show that maltose contains only one of the two carbonyl-groups present in two molecules of dextrose: thus, it forms an osazone with two, instead of four, molecules of phenylhydrazine, and yields a monobasic instead of a dibasic acid. The linking of the two molecules of dextrose must, therefore, involve in the reaction the carbonyl-oxygen of only one molecule. Such a linkage between two monose molecules is called a *monocarbonyl-bond.* If this is denoted by the sign $<$, and a free carbonyl-group in a molecule by $\lessdot$, then maltose can be represented by

$$\underset{\text{Dextrose}}{C_6H_{11}O_5} < \underset{\text{Dextrose}}{O \cdot C_6H_{11}O_5 \lessdot} .$$

Lactose.

214. *Lactose* (*milk-sugar*) is present in milk, and is prepared from it.

> *Whey* is usually employed for this purpose: it is the liquid which remains after the cream has been separated and the skimmed milk has been used for making cheese. In these processes the milk is deprived of most of its fats and proteïns; the whey contains nearly all the lactose, and a large proportion of the mineral constituents of the milk. The lactose is obtained by evaporation, and purified by recrystallization.

Lactose crystallizes in well-defined, large, hard crystals. It has not such a sweet taste as sucrose, and in the mouth resembles sand, on account of the hardness of its crystals.

On hydrolysis, lactose splits up into *d*-galactose and dextrose. It shows the reactions of the monoses, and can be proved, by a method analogous to that employed for maltose, to contain one free carbonyl-group in the molecule: it is, therefore, made up of dextrose and *d*-galactose, linked by a monocarbonyl-bond. The free carbonyl-group belongs to the dextrose molecule, since lactose is converted by oxidation with bromine-water into *lactobionic acid,* which is converted by hydrolysis into *d*-galactose and *d*-gluconic acid. Lactose is, therefore, represented by

$$\underset{d\text{-Galactose}}{C_6H_{11}O_5} < \underset{\text{Dextrose}}{O \cdot C_6H_{11}O_5 \lessdot} .$$

Sucrose.

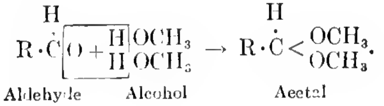
215. *Sucrose* (*cane-sugar* or *saccharose*) is present in many plants, and is prepared from sugar-beet and sugar-cane. It crystallizes well, and is very soluble in water. It melts at 160°, and on cooling solidifies to an amorphous, glass-like mass, which after a considerable time becomes crystalline. When strongly heated, it turns brown, being converted into a substance called *caramel.* On hydrolysis, sucrose yields dextrose and lævulose in equal proportions. This mixture is called *invert-sugar,* and is lævo-rotatory, since lævulose rotates the plane of polarization more to the left (**209**) than dextrose does to the right. Sucrose itself is strongly dextro-rotatory, so that the rotation has been reversed by hydrolysis. This is called *inversion,* a term also applied to the hydrolysis of other dioses and of polyoses. Sucrose does not show the reactions characteristic of the monoses: thus, it does not reduce an alkaline copper solution, is not turned brown by caustic potash, and does not yield an osazone. Hence, it is evident that there are no free carbonyl-groups in its molecule; it may, therefore, be concluded that both of these have entered into reaction in the union of the two monoses. Such a linking between two monoses is called a *dicarbonyl-bond,* and is represented by the sign $<O>$; so that sucrose has the formula

$$\underset{\text{Dextrose}}{C_6H_{11}O_5}<O>\underset{\text{Lævulose}}{C_6H_{11}O_5}.$$

The discovery that alcohols are able, under the influence of hydrochloric acid, to unite with monoses with elimination of water, affords an insight into the nature of the monocarbonyl-bond and the dicarbonyl-bond. The substances thus formed are called *glucosides,* since they are in many respects analogous to the natural glucosides, substances which are decomposed into a sugar, and one or more compounds of various kinds, on boiling with dilute acids. The artificial glucosides are obtained by the action of one molecule of an alcohol upon a monose:

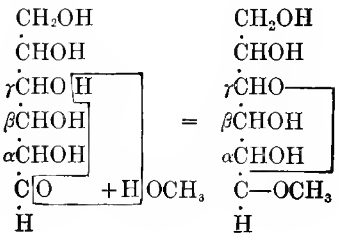
$$C_6H_{12}O_6+CH_3OH = \underset{\text{Methyl glucoside}}{C_6H_{11}O_6\cdot CH_3}+H_2O.$$

These compounds were discovered by Emil Fischer, who has assigned to them a constitution analogous in some respects to that of the acetals (113, 2):



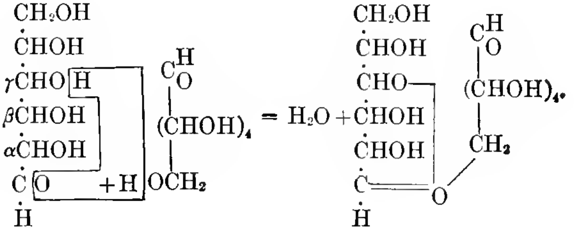
$$\underset{\text{Aldehyde}}{R\cdot\overset{H}{C}}\boxed{O+\begin{matrix}H\\H\end{matrix}}\underset{\text{Alcohol}}{\begin{matrix}OCH_3\\OCH_3\end{matrix}} \rightarrow \underset{\text{Acetal}}{R\cdot\overset{H}{C}<\begin{matrix}OCH_3\\OCH_3\end{matrix}}.$$

In the formation of glucoside, only one molecule of alcohol acts upon the aldose, so that one of the hydroxyl-groups of the latter plays the part of a second alcohol molecule:

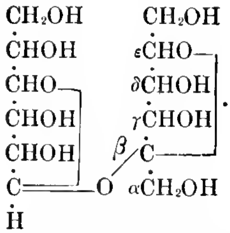


The grounds for the assumption of this constitution are: first, these glucosides are readily resolved into their components, which argues against the existence of a carbon bond between the latter; second, the hydroxyl of the γ-C-atom is assumed to be the one which reacts, since other compounds containing the group —CHOH·CO— do not yield glucosides; the α-hydroxyl-group, therefore, does not react. The γ-hydroxyl, being attached to the fourth C-atom of the chain, is, moreover, the most likely to enter into reaction, since a number of instances of similar behaviour are known, such as that of the acids yielding lactones (187).

The combination of two monoses with elimination of one molecule of water may be represented as being analogous to the formation of a glucoside from an alcohol and a monose. Maltose and lactose, which are united by a monocarbonyl-bond and contain one free carbonyl-group, are combined thus:



By analogy the constitution of sucrose, in which lævulose and dextrose are united by a dicarbonyl-bond, will be



Sucrose forms compounds with bases, called saccharates: among them are $C_{12}H_{22}O_{11} \cdot CaO \cdot 2H_2O$ and $C_{12}H_{22}O_{11} \cdot 2CaO$, which are readily soluble in water. When the solution is boiled, the nearly insoluble tricalcium saccharate $C_{12}H_{22}O_{11} \cdot 3CaO \cdot 3H_2O$ is precipitated.

Manufacture of Sucrose from Sugar-beet.

216. Sucrose is present in solution in the cell-fluid of the sugar-beet. The cell-walls are lined with a thin, continuous layer of protoplasm, constituting a semi-permeable membrane, which prevents the diffusion of the sugar from the cells at ordinary temperatures. When placed in water at 80°–90°, the protoplasm is killed, coagulates, and develops minute ruptures, through which the cell-fluid can diffuse. The process is facilitated by cutting up the beet into pieces 2 to 3 mm. in thickness. In order to make the diffusion-process as complete as possible with a minimum amount of water, the slices are placed in vats through which water circulates in such a manner that the nearly exhausted material is acted on by fresh water, while that which is only partly exhausted comes into contact with the solution already obtained, so that the material richest in sugar is treated with the strongest extract, and *vice versa* (principle of the counter-current). The solution obtained contains 12–15 per cent. of sugar, which is about the proportion contained in the beet itself.

Slaked lime is added to this solution, whereby a double object is attained. First, the free acids in the juice, such as oxalic acid and citric acid, are precipitated, along with the phosphates: their removal is necessary, since on concentrating the solution they would cause inversion. Second, proteïns and colouring matters are precipitated from the solution. To accomplish these objects, it is necessary to add an excess of lime, part of which goes into solution as saccharate. The saccharate is then decomposed by a current of carbon dioxide, care being taken to leave the liquid faintly alkaline. The precipitate is separated by a filter-press, and the filtrate concentrated. To obtain the maximum yield of sugar, the concentration must take place at a low temperature. This is attained by the use of vacuum-pans, in which the sugar-solution boils under diminished pressure. The first product of the concentration is a thick syrup, more strongly alkaline than the original solution. Calcium carbonate is precipitated by repeated treatment with carbon dioxide until the thick syrup is almost neutral. After filtration, the syrup is concentrated until crystals of sugar begin to separate. It is then allowed to cool, when more crystals are obtained, mixed with a syrupy liquid, which is removed in a centrifugal machine. This syrup is further crystallized by slow agitation with a stirring apparatus, and the crystals are again separated by means of the centrifugal machine. The residual syrup (molasses) is worked up in the preparation of alcohol.

The sugar thus prepared is not pure: it is brown, and contains a certain amount of syrup. The crude product is purified by dissolving it, decolourizing with animal-charcoal, and concentrating in vacuum-pans.

Quantitative Estimation of Sucrose.

217. The great practical importance of sucrose makes it desirable to have a quick and accurate method of estimating it quantitatively. This is effected almost exclusively by examining its aqueous solution with the polarimeter (27, 2). Since sucrose is strongly dextro-rotatory ($[\alpha]_D = +66 \cdot 5^\circ$), a small quantity produces an appreciable amount of rotation, which, moreover, is almost independent of the temperature, and for practical purposes may be considered as proportional to the concentration. It is obvious that this method will only yield accurate results when no other optically active substances are present in the solution. If such substances are present, either they must be removed, or their effect taken into account. The former method is adopted in the determination of the amount of sugar in beet. The sample is grated with a fine rasp to destroy the cell-walls, and a weighed quantity is made up to a certain volume with cold water, which dissolves not only the sucrose, but also optically active proteïns. The latter are precipitated with lead acetate, filtered off, and the amount of rotation observed.

When another sugar is present in the solution along with the sucrose, it is necessary to proceed by the second method. Suppose dextrose is the other sugar present. The rotatory power of the solution, which will be dextro-rotatory, is first determined. If it be now inverted, the solution will either diminish in dextro-rotation, or will become lævo-rotatory, since invert-sugar is lævo-rotatory. The rotatory power of an invert-sugar solution obtained from a sucrose solution of given strength being known, these two observations furnish the data by which the percentage of dextrose in cane-sugar or beet-sugar can be calculated.

Velocity of Inversion of Sucrose.

218. The equation for unimolecular reactions (**101**) may be applied to the inversion of a dilute solution of sucrose. If the original amount of the latter present was p, and after a certain time the quantity x has been inverted, then the velocity s in the fraction of time immediately following can be expressed by the equation

$$s=\frac{dx}{dt}=k(p-x),$$

in which k is a constant. The inversion can be effected by means of different acids of the same molecular concentration: the velocity of the reaction is dependent upon the nature of the acid employed, so that different values are obtained for the velocity-constant k. When the values of this constant and of the electrolytic dissociation-constant for these acids are compared, they are found to be proportional to one another. An acid which is ionized strongly effects inversion much more rapidly than one but slightly ionized, from which it follows that only the ionized part of the acid exercises an inverting influence. Since only the hydrogen ion is common to all acids, it must be concluded that *inversion is the result of* *the catalytic action of the hydrogen ions.* Inversely, the concentration of the hydrogen ion in the solutions of acid salts, for example, may be determined by measuring the velocity of inversion.

For an inversion effected by the action of an enzyme, the equation does not hold. This is explained by the fact that the reactivity of an enzyme depends on both the concentration of the sucrose and that of its own inversion-products, whereas the inverting power of an acid is independent of the concentration of the latter.

Fermentation and the Action of Enzymes.

219. The alcoholic fermentation of liquids is one of the longest known reactions. During the nineteenth century a number of other reactions were identified as fermentation-processes, such as the lactic fermentation and butyric fermentation of sugar, putrefactive fermentation, and others. Fermentation-processes include a number of reactions which take place slowly and at ordinary temperatures: they are usually attended by the evolution of a gas and of heat, and depend upon the action of micro-organisms, such as yeast-cells, bacteria, and schizomycetes.

The part played by these micro-organisms in fermentation-processes has been the subject of much diversity of opinion. LIEBIG thought that yeast contained certain easily decomposed ferments, and that it was their decomposition which, as it were, induced the fermentation of the substance. PASTEUR, however, after a series of brilliant researches, became convinced that fermentation can only be brought about by living yeast-cells, and that the process is, therefore, a physiological phenomenon; that is, a complicated biological function of these cells. Thus, he concluded that there could be no fermentation without living yeast-cells, a theory which was universally accepted, LIEBIG's supposition that the part played by the cells is only a secondary one being abandoned.

In accordance with PASTEUR's theory, the process of fermentation is inseparable from the presence and propagation of yeast-cells. If it were found possible to bring about fermentation without their presence, his theory would fall to the ground. EDUARD BUCHNER has effected this. He triturated fresh yeast with sand, whereby the cell-walls were destroyed. The dough-like mass was submitted to great pressure, which expressed a liquid (German, *Presssaft*): this expressed yeast-juice was separated by filtration from the cells still floating in it. BUCHNER proved in various ways that this yeast-juice contains neither living cells nor living protoplasm: for instance, the yeast may be first killed by the action of acetone; the extract from it can nevertheless set up active fermentation in a solution of sugar similarly to that obtained from living yeast. The fermentation is caused by a dissolved substance, which, on account of its properties, such as coagulation on warming, must be classed with proteïns: it is a kind of enzyme, to which BUCHNER has given the name *zymase*. The yeast-cells only have the function of producing zymase.

BUCHNER has proved by analogous methods that other fermentation-processes, such as the lactic fermentation and acetic fermentation, are not caused by the bacilli themselves, but by the enzyme they contain.

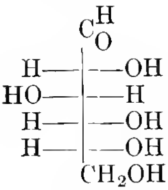
The chemical structure of the enzymes is still wholly unknown. Most of them have not been obtained in the pure state. Their power of decomposing compounds is also not understood. Hitherto, only small insight has been obtained into the conditions upon which their action depends.

First, the enzymes only act at the ordinary, or at a slightly elevated, temperature: below the freezing-point their activity is suspended, but returns at the ordinary temperature: on heating, they are decomposed. Second, they are sometimes rendered inactive ("poisoned") by the presence of small quantities of certain substances, such as hydrocyanic acid. Third, it is very remarkable that a given enzyme can only produce changes in a few substances, and has no action on other similar compounds. Thus, of the different monoses containing two to nine C-atoms, only the trioses, hexoses, and nonoses undergo the alcoholic fermentation: in fact, these are the only monoses which, according to their formula, can be readily converted into CO_2 and C_2H_5OH; for instance,

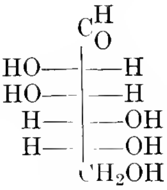
$$C_3H_6O_3 = C_2H_5OH + CO_2.$$

Only the monoses are capable of being fermented by enzymes: dioses must first be converted into monoses. Yeast contains an enzyme, *invertase*, which first decomposes sucrose into a mixture of lævulose and dextrose. This is proved by the fact that certain varieties of yeast, which do not contain invertase, are incapable of fermenting sucrose: thus, *Schizosaccharomyces octosporus*, discovered by Beyerinck, can ferment maltose, but not sucrose. This variety of yeast contains no invertase, but only maltase, the enzyme by which maltose is hydrolyzed.

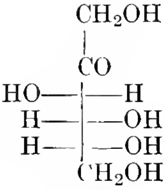
The aptitude for decomposition by enzymes, possessed by the monoses, has been proved by Emil Fischer to be intimately connected with their stereochemical configuration. The three naturally occurring sugars, dextrose, *d*-mannose, and lævulose, are capable of undergoing fermentation, and there is a great similarity in their configurations, since they differ only in the grouping round two C-atoms:



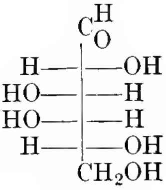
Dextrose



d-Mannose



Lævulose



d-Galactose

d-Galactose, which is also a natural product, has a somewhat different configuration, and is either more slowly fermented by certain varieties of yeast, or not at all. The mirror-images of these compounds, *l*-glucose, etc., are not capable of undergoing fermentation.

The cause of these phenomena is probably the asymmetric structure of the enzyme molecule. Although these substances have not been obtained in the pure state, their great resemblance to the proteïns, and the probability of their formation from them, render their optical activity undoubted: that is, they are to be looked upon as built up of asymmetric molecules. This has led to the hypothesis that there must be a similarity in molecular configuration between the enzymes and the substances which they decompose; and that when this similarity is wanting, no reaction can take place. Emil Fischer appropriately compares this resemblance in structure to that necessary between a lock and a key, in order that the latter may pass the lock.

The application of these views to the chemical processes which go on in the more highly developed organisms leads to the conception that generally in reactions in which proteïns take part, as is undoubtedly the case in the protoplasm, the configuration of the molecule has the same importance as its structure. Various phenomena may be thus explained: the sweet taste possessed by one of the optically active asparagines, and the absence of taste in the other; the different amounts to which the three stereoisomeric tartaric acids are oxidized in the body of a dog fed with them; the fact that, on subcutaneous injection of a rabbit with *l*-arabinose or *d*-arabinose, of the first only 7 per cent., of the latter 36 per cent., is excreted from the body unchanged in the urine; and so on.

Asymmetric Synthesis.

220. Laboratory-syntheses effected with optically inactive material always yield inactive compounds: plants employ such inactive material as carbon dioxide and water for the synthesis of dextro-rotatory dextrose and numerous other optically active compounds. They also produce optically active nitrogenous compounds, such as proteïns and alkaloids, although the nitrogen reacts either in the free state or as nitric acid. Two problems present themselves for solution:

1. The mode of formation of the first optically active substance from inactive material.
2. The production of active substances from inactive material under the influence of an already existing optically active body.

The solution of the first problem is still unattained. It has been suggested that the formation of the first optically active compound took place under the influence of the circularly-polarized light present at the earth's surface; but although this hypothesis is plausible, it still lacks experimental confirmation.

More progress has been made towards the solution of the second problem. Emil Fischer has found that in the cyanohydrin-synthesis (**186**) the use of optically active substances does not always lead to the production of the two possible optical isomerides. An example is furnished by mannose, convertible by the cyanohydrin-synthesis into mannoheptonic acid. From analogy with other cyanohydrin-syntheses, the formation of two stereoisomeric mannoheptonic acids in equal proportions would be anticipated, but only one acid is obtained. It follows that the building-up of a molecule from one already asymmetric can continue in an asymmetric sense. If mannose were converted by a triple application of the cyanohydrin-synthesis into a mannononose, the building-up being in every instance in an asymmetric sense; and if it were possible to decompose this nonose into the original hexose and a product with three carbon atoms, this new substance would also be optically active. One optically active molecule would thus have occasioned the formation of another.

The formation of sugar in plants is probably the result of an analogous process. Dextrose is formed in the chlorophyll-grains, themselves composed of optically active substances. It may be assumed that prior to the formation of sugar these substances combine with carbon dioxide or formaldehyde (**207**, 4), and that the condensation to sugar is asymmetric on account of the asymmetric character of the participating substances.

Some asymmetric syntheses of this type have been effected. Reduction of *benzoylformic acid*, $C_6H_5 \cdot CO \cdot COOH$, yields inactive mandelic acid, $C_6H_5 \cdot CHOH \cdot COOH$. But reduction of an ester of this ketonic acid derived from an optically active alcohol, such as the lævo-rotatory menthol, produces a mixture of the ester of the dextro-acid with a small excess of that of the lævo-acid. On saponification, active mandelic acid is obtained, despite the elimination of the asymmetric structure occasioned by the menthol-residue. The formation of *l*-lactic acid by the reduction of *l*-bornyl pyroracemate with aluminium-amalgam is a similar reaction:

$$\underset{l\text{-Bornyl pyroracemate}}{CH_3 \cdot CO \cdot COOC_{10}H_{17}} \rightarrow \underset{l\text{-Lactic acid}}{CH_3 \cdot CHOH \cdot COOH.}$$

Another example is the formation of excess of *l*-tartaric acid by treating monobornyl fumarate with permanganate.

The occurrence in nature of all the possible optical isomerides of a compound is exceptional. Only the dextro-rotatory forms of dextrose, tartaric acid, and lactic acid are natural products. Why nature has not produced the chemical mirror-images of all optically active substances found in the existing flora and fauna, since, as far as is at present known, the probability for the formation of both must have been equal, is a problem by no means solved.

III. POLYOSES.

Raffinose, $C_{18}H_{32}O_{16}+5H_2O$.

221. *Raffinose* is the most important of the hexotrioses, of which but few are known. Their formula is $C_{18}H_{32}O_{16}$; that is,

$$3C_6H_{12}O_6-2H_2O.$$

Raffinose is a hexotriose, since, on hydrolysis, it takes up two molecules of water with formation of an equal number of molecules of lævulose, dextrose, and *d*-galactose. By careful hydrolysis, raffinose can be split up quantitatively into lævulose and a diose (*melediose*): from the latter, dextrose and *d*-galactose can be obtained, in the same way as from lactose, with which, however, melediose is not identical. Raffinose exhibits none of the monose reactions: thus, it does not reduce an alkaline copper solution. This proves the absence of a free carbonyl-group, so that raffinose must be represented by

$$C_6H_{11}O_5{<}O\cdot C_6H_{10}O_4{<}O{>}C_6H_{11}O_5.$$

Melediose exhibits the sugar reactions, and therefore contains one free carbonyl-group, so that its formula is

$$C_6H_{11}O_5{<}O\cdot C_6H_{11}O_5{<},$$

which proves that the decomposition of raffinose into monose and diose takes place at the dicarbonyl-bond, as otherwise there would have been obtained a diose, $C_6H_{11}O_5{<}O{>}C_6H_{11}O_5$, lacking a free carbonyl-group.

Raffinose crystallizes with five molecules of water. When sucrose contains a certain proportion of this polyose, it yields pointed crystals.

Manneotetrose is a tetrose present in manna. On hydrolysis it yields two molecules of galactose, one molecule of dextrose, and one molecule of lævulose:

$$\underset{\text{Manneotetrose}}{C_{24}H_{42}O_{21}}+3H_2O=\underset{\text{Galactose}}{2C_6H_{12}O_6}+\underset{\text{Dextrose}}{C_6H_{12}O_6}+\underset{\text{Lævulose}}{C_6H_{12}O_6}.$$

Higher Polyoses.

222. Most of the higher polyoses are amorphous, and do not possess a sweet taste: many of them are insoluble in water. On hydrolysis, they yield monoses, either pentoses or hexoses, so that it may be assumed that the monose-residues are united by the oxygen atom. The molecular weight of the polyoses is unknown, but must be very great. Their formula may be represented as being derived thus:

$$nC_6H_{12}O_6-(n-1)H_2O.$$

If n is very great, this constitution approximates to

$$nC_6H_{12}O_6-nH_2O = n(C_6H_{10}O_5),$$

which is the formula indicated by the results of analysis. On hydrolysis, nearly all the polyoses yield monoses with the same number of C-atoms: a polyose which can be hydrolyzed to a pentose and a hexose seems, however, to be present in the mucus of plants, such as linseed.

Starch.

223. *Starch* is the first observable assimilation-product of plants. It occurs in large quantities in the tubers, roots, and seeds of many plants, in which it is present in the form of granules differing in form and size in different plants. Some of these granules are represented in Figs. 67, 68, and 69.

Starch is insoluble in cold water: in hot water it swells up without dissolving. It yields an intense blue coloration with a dilute solution of iodine, for which this reaction serves as a test. When boiled with dilute acids, starch is converted into dextrose. On treatment with diastase, starch-paste first liquefies, its molecules then decompose, and ultimately maltose and *iso*maltose, $C_{12}H_{22}O_{11}$, are formed. Both these methods of treatment yield intermediate products, however: they are gum-like substances, polyoses containing a smaller number of atoms in the molecule than starch, called *dextrins*. Dextrin is also obtained by heating starch alone, or to 110° with a small quantity of nitric acid.

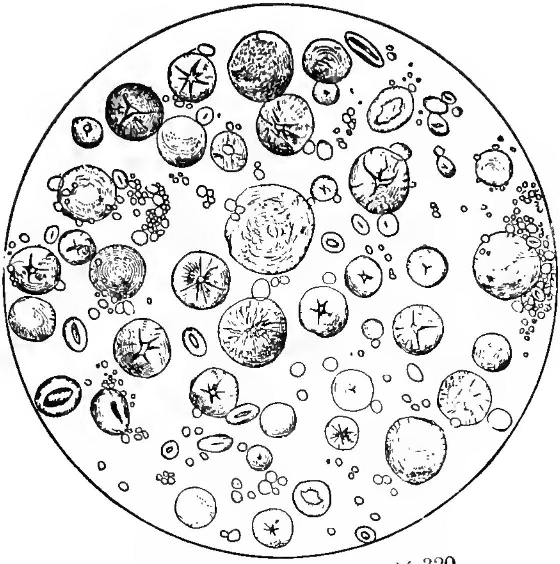


Fig. 67.—Rye-starch. × 320.

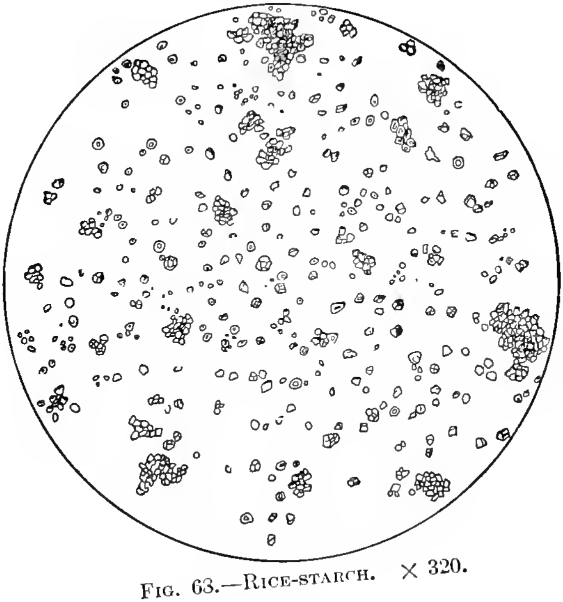


Fig. 63.—Rice-starch. × 320.

Starch does not show any of the reactions of the monoses: it does not reduce an alkaline copper solution, nor resinify with alkalis, and yields no compound with phenylhydrazine. This proves the absence of a free carbonyl-group, so that its molecule must be represented by

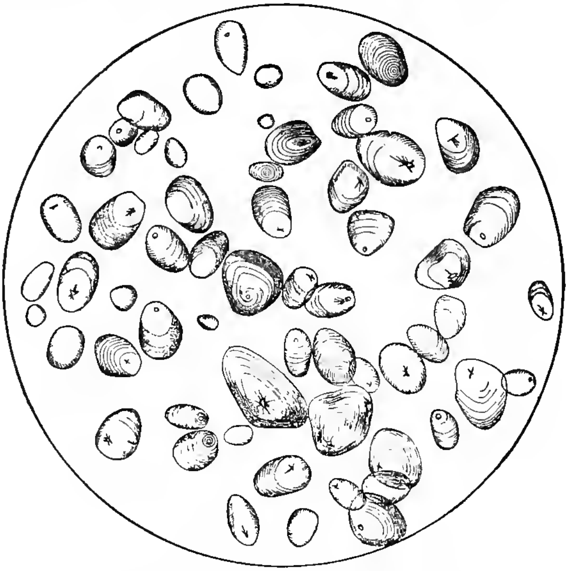


Fig. 69.—Potato-starch. × 250.

$$C_6H_{10}O_5<O\ldots\ldots C_6H_{10}O_4<O>C_6H_{10}O_4\ldots\ldots O>C_6H_{10}O_5.$$

It might be suggested that the molecule of starch contains more than one dicarbonyl-bond, when the formula would be, for example,

$$C_6H_{10}O_5<O\ldots\ldots C_6H_{10}O_4<O>C_6H_{10}O_4\cdot O>C_6H_{10}O_5\ldots\ldots O>$$
$$>C_6H_{10}O_4<O>C_6H_{10}O_4\cdot O>C_6H_{10}O_5\cdot O>C_6H_{10}O_5\ldots\ldots O>C_6H_{10}O_5.$$

It does not, since hydrolysis of a compound of this type must yield, in addition to dextrose, a substance $>C_6H_{12}O_6<$, containing two free carbonyl-groups, and no such product has been obtained by the hydrolysis of starch.

Dextrin can unite with phenylhydrazine, and exhibits the reactions of the monoses, such as reduction of an alkaline copper solution, and the formation of a yellow coloration with alkalis. It must, therefore, be assumed to contain a free carbonyl-group.

Manufacture of Starch.

224. The process by which starch is manufactured is theoretically very simple. Potato-starch is prepared by first grinding the potatoes fine, whereby the cell-tissue is destroyed The starch-granules, thus laid bare, are washed out of the cell-tissue by treatment with water in a specially constructed apparatus, somewhat resembling a sieve. They are allowed to settle on standing, are then carefully washed, and finally dried slowly.

Starch is employed for many purposes in the arts, as an adhesive paste, and for stiffening linen in laundries. In the latter process, the starch-paste is converted by the heat of the smoothing-iron into a stiff, shining layer of dextrin, coating the fibres of the linen. Starch is of great importance as a large constituent of foods. It is more fully dealt with in this connection in physiological text-books.

Glycogen, $(C_6H_{10}O_5)_x$.

225. *Glycogen* is a substance resembling starch, and is present in the animal organism: the other polyoses are vegetable products. It is usually prepared from liver, and is a white, amorphous powder, dissolving in water with formation of an opalescent solution. On hydrolysis, it yields only dextrose. Apparently there are different kinds of glycogen, according to the animal from which it is isolated.

Cellulose, $(C_6H_{10}O_5)_x$.

226. *Cellulose* is a polyose of very high molecular weight. The cell-walls of plants consist principally of this substance, together with *lignin*, which is probably not a polyose. Cellulose is very stable towards dilute acids and alkalis, a property which is made use of in the technical preparation of cellulose, in order to free it from the substances present along with it in the plant-material. *Linen, cotton,* and *paper* consist almost exclusively of cellulose: pure filter-paper is nearly chemically pure cellulose. When it is dissolved in strong sulphuric acid, and the solution boiled, after dilution with water, it is completely hydrolyzed. Cellulose from cotton-wool, paper, etc., yields exclusively dextrose; from coffee-beans, cocoa-nibs, etc., *d*-mannose. Cellulose is converted by treatment with sulphuric acid containing half its volume of water into a colloidal modification, *amyloid,* which gives a blue coloration with

iodine: this reaction furnishes a test for cellulose. The latter is soluble in an ammoniacal solution of copper oxide (SCHWEITZER'S reagent): from this solution it is precipitated chemically unchanged by acids and salts, and forms an amorphous powder when dried.

Technical Applications of Cellulose.

227. *Linen* is prepared from the stalk of the flax-plant. The linen fibres can be obtained from the flax, cellulose being very stable towards chemical reagents. For example, the flax is steeped in water for from ten days to a fortnight. The consequent decay of the external fibre gives rise to an unpleasant smell. The material is then dried by spreading it out, and passed between corrugated rollers. This loosens the external woody fibre, which is then stripped off by revolving wooden arms named "wipers," a process called "scutching." The linen-fibres have a grey colour, and are bleached by either being spread out in the open or by means of bleaching-powder.

Paper was formerly prepared almost exclusively from linen-rags, but is now largely manufactured from wood and straw, which must be divided into fibres, and these separated as much as possible from the other, so-called incrusting, substances present. This is effected by the *sulphite-method*, in which the wood is heated under pressure with a solution of calcium hydrogen sulphite. When straw is used, it is heated with caustic soda under pressure. By these processes most of the incrusting substances are dissolved, and the wood or straw bleached at the same time: the cellulose which remains can be readily separated into fine fibres, which is necessary to the manufacture of paper-pulp. It is not, however, possible to remove all the lignin by these means; in consequence, wood-paper and straw-paper answer to the tests for lignin, and can be recognized thereby. Lignin gives a yellow coloration with salts of aniline (**313**), and a red coloration with a solution of phloroglucinol (**354**) in concentrated hydrochloric acid.

Parchment-paper is prepared by converting the outer surface of paper into amyloid (**226**), a process which imparts toughness to it.

Nitrocelluloses.

228. The *nitrocelluloses* are of great technical importance. When cotton-wool is treated with a mixture of nitric and sulphuric acids, a mixture of *mononitrocellulose, dinitrocellulose,* and *trinitrocellulose* is obtained, the extent of the nitration being dependent upon the concentration of the acids and the duration of the process. Cellulose is arbitrarily assumed to have the molecular formula $C_6H_{10}O_5$. In the nitration of cellulose the final product is trinitro-oxycellulose. For, on treatment with ferrous chloride, trinitro-oxycellulose yields *oxycellulose*, but no cellulose, proving that the formation of the trinitro-compound is accompanied by oxidation of the cellulose; whereas nitro-mannitol, for example, is reconverted by this reagent into mannitol, without oxidation of the latter. Oxycellulose has the formula

$$(C_{24}H_{40}O_{21})_x \quad \text{or} \quad [(C_6H_{10}O_5)_3+(C_6H_{10}O_6)]_x;$$

and its trinitro-derivative is

$$[C_6H_7(NO_2)_3O_5]_3+C_6H_7(NO_2)_3O_6.$$

The solution in a mixture of alcohol and ether of mononitrocellulose and dinitrocellulose is known as *collodion:* on evaporation it leaves an elastic skin, and is employed in photography. The trinitrocellulose is *guncotton*, which looks like cotton-wool, but feels somewhat rough to the touch, and is extensively employed as an explosive. It burns quietly when a loose tuft of it is ignited, but can be made to explode by the detonation of a small quantity of mercury fulminate, and yields only gaseous products, nitrogen, hydrogen, water-vapour, carbon monoxide, and carbon dioxide. It exerts a detonating or *brisant* (160) action, and without modification is, therefore, unsuitable for use in artillery.

When guncotton is dissolved in acetone or ethyl acetate, a gelatinous mass is obtained: after removal of the solvent, an amorphous, transparent substance is left, having the same chemical composition as guncotton, but burning and exploding more slowly. The velocity of explosion of guncotton being thus moderated, it is made available in this form for use in artillery, under the name of "smokeless powder."

Trinitrocellulose is also employed in the manufacture of *artificial silk*. In DE CHARDONNET's method, the nitrate is dissolved in a mixture of alcohol and ether, and the solution pressed through fine glass tubes at a pressure of forty to fifty atmospheres. The filaments are received in water, which takes up the solvent, leaving a very fine thread: when ten to twenty of these are spun together, a thread capable of being woven is obtained. When the fabric thus prepared is treated with a solution of calcium sulphide, obtained from the tank-waste in the manufacture of sodium carbonate by the LE BLANC process ("Inorganic Chemistry," 226), the NO_2-groups of the nitro-compound are eliminated, with production of nearly pure cellulose in a form exactly resembling silk.

AMINO-ACIDS.

229. The *amino-acids* contain one or more amino-groups in direct union with carbon. They are of physiological importance, since many are decomposition-products of proteïns, and some are natural products. They are synthesized by several methods.

1. By the action of the halogen-substituted fatty acids on ammonia, a method analogous to the formation of amines:

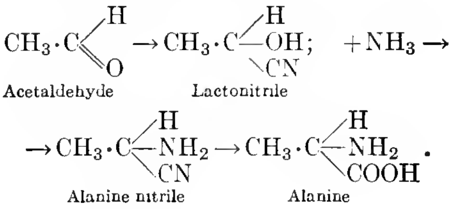
$$H_2N\boxed{H+Cl}H_2C\cdot COOH = H_2N\cdot CH_2\cdot COOH + HCl.$$

2. By reduction of oximes with sodium amalgam:

$$R\cdot C(NOH)\cdot COOH + 4H = R\cdot CHNH_2\cdot COOH + H_2O.$$

This is a method of converting ketonic acids into amino-acids.

3. α-Amino-acids are formed by the action of ammonia upon the cyanohydrins of aldehydes or ketones, and subsequent hydrolysis of the nitrile-group (STRECKER):



$$\underset{\text{Acetaldehyde}}{CH_3\cdot C\begin{matrix}\diagup H\\ \diagdown O\end{matrix}} \rightarrow \underset{\text{Lactonitrile}}{CH_3\cdot C\begin{matrix}\diagup H\\ -OH;\\ \diagdown CN\end{matrix}} \quad + NH_3 \rightarrow$$

$$\rightarrow \underset{\text{Alanine nitrile}}{CH_3\cdot C\begin{matrix}\diagup H\\ -NH_2\\ \diagdown CN\end{matrix}} \rightarrow \underset{\text{Alanine}}{CH_3\cdot C\begin{matrix}\diagup H\\ -NH_2\\ \diagdown COOH\end{matrix}}.$$

The amino-acids possess two opposite characters: they form salts with both bases and acids, and are therefore both basic and acidic simultaneously.

Replacement of the hydrogen of the amino-group by radicals yields amino-acids of a more complicated character. Thus, like ammonia, with acid chlorides they yield an acid amide with one hydrogen atom of the amino-group replaced:

$$R\cdot CO\boxed{Cl+H}HN\cdot CH_2\cdot COOH = R\cdot CO\cdot NH\cdot CH_2\cdot COOH+HCl.$$

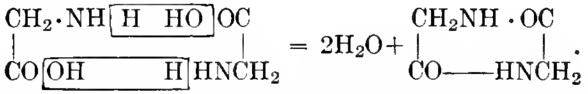
Compounds of this kind are therefore both amino-acids and acid amides.

Amino-acids with the hydrogen of the amino-group replaced by alkyl-groups are also known. They are obtained by the action of amines, instead of ammonia, on the halogen-substituted acids:

$$(CH_3)_2N\boxed{H+Cl}H_2C\cdot COOH = (CH_3)_2N\cdot CH_2\cdot COOH+HCl.$$

The amino-acids undergo most of the decompositions characteristic of amines; thus, with nitrous acid they yield hydroxy-acids, just as the amines yield alcohols.

Like those of the halogen-substituted acids and hydroxy-acids (178 and 183), the properties of the amino-acids depend on the position of their characteristic group—the amino-group—relative to the carboxyl-group. The α-amino-acids readily yield anhydrides (acid amides) by the elimination of two molecules of water from two molecules of acid:

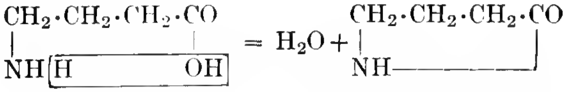


$$\begin{array}{l} CH_2\cdot NH\boxed{H\quad HO}OC \\ |\qquad\qquad\qquad\quad | \\ CO\boxed{OH\qquad\quad H}HNCH_2 \end{array} = 2H_2O+ \begin{array}{l} CH_2NH\cdot OC \\ |\qquad\qquad\quad | \\ CO\text{——}HNCH_2 \end{array}.$$

The β-amino-acids easily lose ammonia, with formation of unsaturated acids. Thus, β-aminopropionic acid, obtained from β-iodopropionic acid, is converted by heat into acrylic acid and ammonia:

$$\boxed{NH_2}\cdot CH_2\cdot CH\boxed{H}\cdot COOH = NH_3+CH_2{:}CH\cdot COOH.$$

Like the γ-hydroxy-acids, the γ-amino-acids yield inner anhydrides. On account of their similarity to the lactones, these substances are called *lactams:*



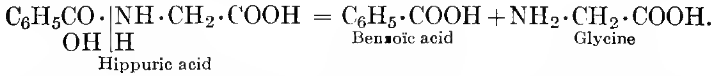
$$\begin{array}{l} CH_2\cdot CH_2\cdot CH_2\cdot CO \\ |\qquad\qquad\qquad\quad | \\ NH\boxed{H\qquad\quad OH} \end{array} = H_2O+ \begin{array}{l} CH_2\cdot CH_2\cdot CH_2\cdot CO \\ |\qquad\qquad\qquad\quad | \\ NH\text{————}\rfloor \end{array}$$

γ-Aminobutyric acid   Lactam of γ-aminobutyric acid

Emil Fischer proved that the *esters of amino-acids* can be obtained by the ordinary method, dissolving the acids in absolute alcohol and treating this solution with hydrochloric-acid gas (97). Hydrochlorides are the primary products, the amino-group in these esters retaining its basic character: an example is the *ethyl ester of glycine hydrochloride*, $C_2H_5OOC\cdot CH_2\cdot NH_2\cdot HCl$. The esters are prepared by treating aqueous solutions of the hydrochlorides with concentrated potassium hydroxide at a low temperature, and immediately extracting with ether. Emil Fischer found these esters well adapted for the purification and separation of amino-acids. This is of great importance in the chemistry of proteïns, which are resolved into a mixture of such acids by the action of acids or bases.

Individual Members.

230. *Glycine* (glycocoll or aminoacetic acid), $NH_2\cdot CH_2\cdot COOH$, can be obtained by boiling glue with dilute sulphuric acid or with barium hydroxide: it owes the name "glycocoll" to this method of formation, and to its sweet taste (*γλυκύς*, sweet; *κόλλα*, glue). It is also prepared from *hippuric acid*, a constituent of the urine of horses. Hippuric acid is glycine with one hydrogen atom of the amino-group replaced by benzoyl, C_6H_5CO; and it therefore has the formula $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH$. Like all acid amides, it is decomposed by boiling with dilute acids, with addition of the elements of water:

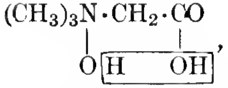


$$\underset{\text{Hippuric acid}}{\begin{array}{r|l} C_6H_5CO\cdot & NH\cdot CH_2\cdot COOH \\ OH & H \end{array}} = \underset{\text{Benzoïc acid}}{C_6H_5\cdot COOH} + \underset{\text{Glycine}}{NH_2\cdot CH_2\cdot COOH.}$$

Glycine can be synthetically prepared by the action of ammonia on monochloroacetic acid.

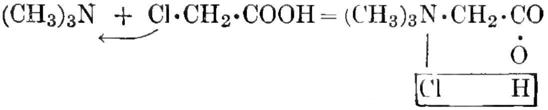
Glycine is a crystalline solid, and melts at 232° with decomposition: it is very readily soluble in water, and insoluble in absolute alcohol. Like many amino-acids, it forms a well-crystallized, blue copper salt, soluble with difficulty in water, and obtained by boiling copper carbonate with a solution of glycine. This derivative crystallizes with one molecule of water of crystallization, and has the formula $(NH_2\cdot CH_2\cdot COO)_2Cu + H_2O$.

Betaïne, $C_5H_{11}O_2N$, is a derivative of trimethylglycine: it is found in the juice of the sugar-beet, and accumulates in the molasses during the manufacture of sugar. It is an inner ammonium salt,



$$\begin{array}{l}(CH_3)_3N\cdot CH_2\cdot CO\\ \qquad\quad |\qquad\quad |\\ \qquad\quad O\boxed{H\quad OH}\end{array},$$

since it is synthetically obtained from trimethylamine by the action of monochloroacetic acid, with elimination of HCl:



$$\begin{array}{l}(CH_3)_3N + Cl\cdot CH_2\cdot COOH = (CH_3)_3N\cdot CH_2\cdot CO\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |\qquad\quad O\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \boxed{Cl\qquad H}\end{array}$$

This reaction is analogous to the interaction of alkyl halides and tertiary amines to form the salts of quaternary ammonium bases (71).

Betaïne yields large crystals with one molecule of water, which it loses at 100°, or when allowed to stand over sulphuric acid. On heating it decomposes, with formation of trimethylamine.

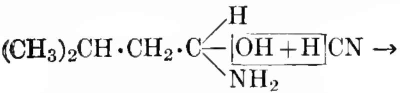
Many tertiary amines can be converted into substances with a constitution analogous to that of betaïne; that is, inner salts of ammonium bases. These compounds are called *betaïnes*.

Alanine, or α-aminopropionic acid, $CH_3\cdot CH(NH_2)\cdot COOH$, is synthetically prepared by the action of ammonia on α-chloropropionic acid.

Leucine, or α-amino*iso*butylacetic acid,

$$(CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot COOH,$$

results along with glycine from the decomposition of proteïns by the action of acids or alkalis, or by putrefaction. It is synthetically obtained from *iso*valeraldehyde-ammonia by the action of hydrocyanic acid, and hydrolysis of the resulting nitrile:



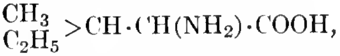
$$(CH_3)_2CH\cdot CH_2\cdot C\begin{cases}H\\ \boxed{OH+H}CN\\ NH_2\end{cases}\rightarrow$$

*iso*Valeraldehyde-ammonia

$$\rightarrow (CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot CO_2H.$$

Leucine

iso*Leucine*, or α-amino-β-methylvaleric acid,



$$\begin{matrix}CH_3\\ C_2H_5\end{matrix}>CH\cdot CH(NH_2)\cdot COOH,$$

is also a decomposition-product of proteïns. Its constitution is proved by synthesis. The aldehyde formed by oxidation of secondary butylcarbinol—the optically active amyl alcohol—yields by the method of **229**, 3, an amino-acid identical with *iso*leucine.

Fusel-oil is a by-product in the alcoholic fermentation (**47**). EHRLICH has proved that it is not derived from the sugars, but from leucine and *iso*leucine formed by decomposition of the proteïns present in the fermenting liquid. These proteïns are constituents of the grain, potatoes, and other material employed in the manufacture of alcohol. When sugar is fermented with a pure yeast-culture in presence of leucine, *iso*butylcarbinol is formed as a by-product: with *iso*leucine secondary butylcarbinol results. These two amyl alcohols are the principal constituents of fusel-oil (**51**).

The leucine obtained from proteïns is optically active: its formula contains an asymmetric carbon atom.

231. *Asparagine* is often present in sprouting seeds; to the extent of 20–30 per cent. in dried lupine-seeds. It is *aminosuccinamic acid*, $C_2H_3(NH_2)<\begin{smallmatrix}CONH_2\\COOH\end{smallmatrix}$, since on hydrolysis it is converted into *aminosuccinic acid* (*aspartic acid*), $COOH\cdot CH(NH_2)\cdot CH_2\cdot COOH$, the structure of which is inferred from its conversion into malic acid by treatment with nitrous acid. Asparagine prepared from seeds is sometimes dextro-rotatory, but generally lævo-rotatory. The former is sweet, the latter tasteless.

Homologous with asparagine is *glutamine*, a constituent of the seeds of sprouting plants. It is the amic acid (**165**) of α-aminoglutaric acid, $COOH\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot COOH$.

In addition to the monoamino-acids, diamino-acids are also obtained by decomposing proteïns with acids. Some of them merit description.

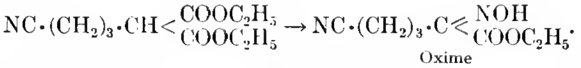
Lysine, $C_6H_{14}O_2N_2$, is decomposed by putrefaction-bacilli with formation of pentamethylenediamine (**162**): it has the formula $NH_2\cdot CH_2\cdot(CH_2)_3\cdot CH<\begin{smallmatrix}NH_2\\COOH\end{smallmatrix}$, and is an $\alpha\varepsilon$-aminocaproïc acid.

EMIL FISCHER has proved this formula by synthesis. On bringing ethyl monosodiomalonate into contact with γ-chlorobutyronitrile, *ethyl γ-cyanopropylmalonate* is formed:

$$\underset{\text{Ethyl monosodiomalonate}}{(COOC_2H_5)_2CHNa}+\underset{\gamma\text{-Chlorobutyronitrile}}{Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN}\rightarrow$$

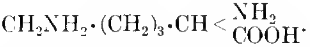
$$\rightarrow\underset{\text{Ethyl }\gamma\text{-cyanopropylmalonate}}{(COOC_2H_5)_2CH\cdot(CH_2)_3\cdot CN.}$$

Treatment with ethyl nitrite and sodium ethoxide converts this ester by elimination of a carbethoxyl-group into the sodium salt of an oxime:



$$NC\cdot(CH_2)_3\cdot CH<\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}\rightarrow \underset{\text{Oxime}}{NC\cdot(CH_2)_3\cdot C\leqslant\begin{matrix}NOH\\COOC_2H_5\end{matrix}}.$$

Reduction of this oxime with sodium and alcohol converts the NOH-group into NH_2, and the CN-group into CH_2NH_2, with formation of inactive lysine,



$$CH_2NH_2\cdot(CH_2)_3\cdot CH<\begin{matrix}NH_2\\COOH\end{matrix}.$$

Ornithine is the next lower homologue of lysine, and has the formula $C_5H_{12}O_2N_2$ or $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH$. Bacteria convert it into putrescine or tetramethylenediamine (162). Its structure is proved by Emil Fischer's synthesis (371).

THE WALDEN INVERSION.

232. When one group attached to an asymmetric carbon atom is replaced by another, it is impossible to predict the sign of the rotation of the new compound: sometimes it is the same as that of the original substance, and sometimes opposite to it. By a series of substitutions, Walden has transformed an optically active compound into its optical antipode. On treatment with moist silver oxide, *l*-chlorosuccinic acid was converted into *l*-malic acid, and this substance was transformed by means of phosphorus pentachloride into *d*-chlorosuccinnic acid On the other hand, starting from *d*-chlorosuccinic acid, the same operation yielded *l*-chlorosuccinic acid. These transformations are indicated in the cyclic scheme

$$\begin{tikzcd}
\textit{l}\text{-Chlorosuccinic acid} \arrow[r, "AgOH"] & \textit{l}\text{-Malic acid} \arrow[d, "PCl_5"] \\
\textit{d}\text{-Malic acid} \arrow[u, "PCl_5"'] & \textit{d}\text{-Chlorosuccinic acid.} \arrow[l, "AgOH"']
\end{tikzcd}$$

Obviously, a transposition of the groups attached to the asymmetric carbon atom is induced either by the moist silver oxide or by the phosphorus pentachloride.

The following is another reaction-cycle, worked out by Emil Fischer:

$$\begin{tikzcd}
\textit{d}\text{-Alanine} \arrow[r, "NOBr"] & \textit{l}\text{-Bromopropionic acid.} \arrow[d, "NH_3"] \\
\textit{d}\text{-Bromopropionic acid} \arrow[u, "NH_3"'] & \textit{l}\text{-Alanine.} \arrow[l, "NOBr"']
\end{tikzcd}$$

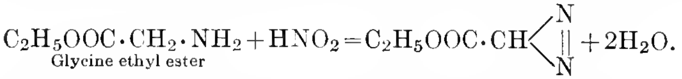
Here the transposition probably took place during the replacement of the amino-group by bromine under the influence of nitrosyl bromide and not by the action of ammonia, since, with widely different experimental conditions, the same product with a similar sign of rotation always resulted in the latter operation. Although *d*-alanine reacted with nitrosyl bromide to form *l*-bromopropionic acid, its ester under identical conditions yielded *d*-bromopropionic acid.

Nitrosyl bromide, however, converted *l*-valine or α-amino*iso*valeric acid, $(CH_3)_2CH\cdot CHNH_2\cdot COOH$, into an active bromovaleric acid, from which ammonia regenerated *l*-valine. In this instance, therefore, it must be assumed either that transposition is not caused by the nitrosyl bromide, or else that it occurs in both reactions. Other examples of the replacement of halogens by the amino-group under the influence of ammonia, explicable only by the assumption of a transposition, have been observed by Emil Fischer.

The obvious complexity of the Walden inversion renders it necessary to accept with great caution all predictions as to the configuration of any new compound resulting from substitution at an asymmetric carbon atom.

ETHYL DIAZOACETATE.

233. Curtius has obtained a yellow oil of characteristic odour by the action of nitrous acid on the ethyl ester of glycine: this substance has the formula $C_4H_6O_2N_2$, and explodes when heated. The method of its formation is indicated in the following equation:

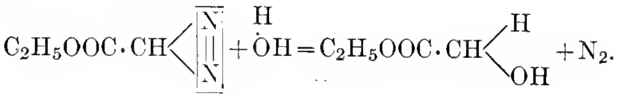


$$\underset{\text{Glycine ethyl ester}}{C_2H_5OOC\cdot CH_2\cdot NH_2} + HNO_2 = C_2H_5OOC\cdot CH\Big\langle\begin{matrix}N\\ \|\\ N\end{matrix} + 2H_2O.$$

It is *ethyl diazoacetate*, and is also called *diazoacetic ester*.

The structural formula indicated is proved by numerous transformations: they can be classified in three divisions.

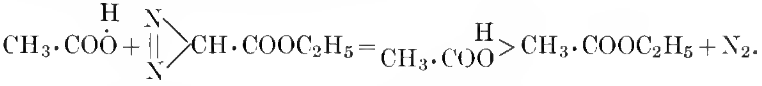
I. The first group includes the reactions involving the elimination of the diazo-nitrogen. As an example may be cited the conversion of ethyl diazoacetate into ethyl glycollate by treatment with dilute acids:



$$C_2H_5OOC\cdot CH\Big\langle\boxed{\begin{matrix}N\\ \|\\ N\end{matrix}} + \overset{H}{O}H = C_2H_5OOC\cdot CH\Big\langle\begin{matrix}H\\ \\ OH\end{matrix} + N_2.$$

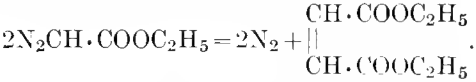
BREDIG discovered that this reaction is greatly accelerated by the catalytic agency of hydrogen ions, and on this observation he has based one of the best methods for the detection and quantitative estimation of such ions.

Concentrated hydrochloric acid yields analogously ethyl monochloroacetate, and iodine ethyl di-iodoacetate. Organic acids produce acidylglycollic acid esters:



$$CH_3\cdot CO\overset{H}{\dot{O}} + \begin{matrix}N\\ \|\\ N\end{matrix}\!\!>CH\cdot COOC_2H_5 = \begin{matrix}H\\ CH_3\cdot COO\end{matrix}\!\!>CH_3\cdot COOC_2H_5 + N_2.$$

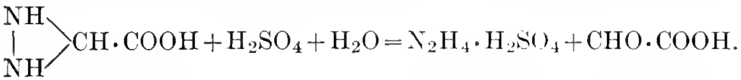
Near its boiling-point ethyl diazoacetate loses all its nitrogen, with formation of ethyl fumarate:



$$2N_2CH\cdot COOC_2H_5 = 2N_2 + \begin{matrix}CH\cdot COOC_2H_5\\ \|\\ CH\cdot COOC_2H_5\end{matrix}.$$

II. In the second group of reactions the nitrogen is not evolved as gas, but one of the bonds between the diazo-group and carbon is severed, with formation of pyrazole-derivatives (461).

III. The third group comprises addition-reactions involving the transformation of the double bond between the nitrogen atoms into a single bond. An example is the addition of hydrogen to form *hydrazinoacetic acid*, a compound decomposed by acids at the ordinary temperature into glyoxylic acid and a hydrazine salt:



$$\begin{matrix}NH\\ |\\ NH\end{matrix}\!\!>CH\cdot COOH + H_2SO_4 + H_2O = N_2H_4\cdot H_2SO_4 + CHO\cdot COOH.$$

Hydrazinoacetic acid　　Hydrazine sulphate　　Glyoxylic acid

The hydrogen atom of the CHN_2-group is replaceable by metals, sodium dissolving in ethyl diazoacetate with evolution of hydrogen.

PROTEÏNS.

234. *Proteïns* are compounds of great importance in the animal and vegetable kingdoms, but of such complex structure that their chemical investigation is a matter of extreme difficulty. Their great physiological importance is made apparent by the fact that the dry material in animal bodies—apart from the mineral constituents and fats—consists almost wholly of proteïns, by their being an essential constituent of each living plant-cell, and by their forming the most important part of human and animal food. An animal can exist without fats and carbohydrates for a protracted period, but its death is assured by the withdrawal of proteïns from its nourishment.

The investigation of the proteïns is rendered difficult not only by their complex structure, but also by the fact that, with few exceptions, they do not crystallize, and cannot be distilled without undergoing decomposition, so that advantage cannot be taken of these valuable aids in the isolation of individual substances. Moreover, many proteïns change very readily into other substances, and the distinctions between the different varieties are sometimes by no means well defined.

A number of groups of nitrogenous compounds are classed as *proteïns*. Since they sometimes exhibit great differences in physical and chemical behaviour, it is necessary first to state the general properties characteristic of them. They contain only five elements, and do not differ much from one another in composition, as the table indicates.

Carbon	50–55	per cent.
Hydrogen	6·5–7·3	”
Nitrogen	15–17·6	”
Oxygen	19–24	”
Sulphur	0·3–5	”

Those of one variety, called *phosphoproteïns*, also contain phosphorus.

235. The solutions of all proteïns are optically active and lævorotatory. The proteïns are colloids (" Inorganic Chemistry," **196**); they are, therefore, unable to diffuse through parchment-paper. Advantage is often taken of this property in separating them from salts and other crystalloids (*loc. cit.*). Some of them have been obtained crystalline, among them *serum-albumin:* most of them are white, amorphous powders without definite melting-points. On heating, they carbonize, with evolution of gases.

Many, but not all proteïns can be " salted out " from solution. This " salting-out " is an important aid in identifying and separating the different varieties: usually common salt or magnesium sulphate is employed. It is remarkable that all proteïns can be completely salted out from their solutions in both neutral and acid liquids by saturation with ammonium sulphate. The albumins can be fractionally precipitated from aqueous solutions by gradually increasing the concentration of the ammonium-sulphate solution. The point of concentration at which a salt begins to precipitate a proteïn is just as characteristic for the latter as, for example, the solubility is for a crystalline substance. When the salting-out is effected at ordinary temperatures, it causes no change in the properties of the proteïns: their solubilities after the operation are the same as before it.

Addition of alcohol precipitates proteïns unchanged from aqueous solution: strong alcohol *coagulates* them, as also does boiling with water. For each albumin there is a definite coagulation-point: in other words, each albumin coagulates at a definite temperature. On coagulation, the differences in solubility between the proteïns vanish: all are rendered insoluble in neutral solvents, and can be brought into solution again only by treatment with dilute caustic alkalis or with mineral acids. A solution, which behaves exactly like the solutions thus obtained, can be prepared by boiling uncoagulated albumins with a large excess of acetic acid or caustic alkali.

In this process the albumins undergo a change called *denaturation*. They cease to be coagulable by heat, but their composition remains unaltered. The products are called *meta-proteïns*. When the hydrolysis was effected with alkali, the product was formerly termed an *albuminate* or *alkali-albumin*, when an acid was employed, a *syntonin* or *acid-albumin*. The meta-proteïns are insoluble in water, but soluble in dilute acids and alkalis. They are precipitated by neutralizing their solutions.

The proteïns are precipitated from solution by various substances, either by coagulation or by the formation of compounds insoluble in water. Coagulation is effected by the addition of mineral acids, preferably nitric acid.

The formation of compounds insoluble in water results on addition of salts of most of the heavy metals, especially copper sulphate, ferric chloride, and an acidified solution of mercuric chloride. The proteïns, therefore, behave like weak acids, which with the oxides of these metals yield compounds of the nature of salts.

Some weak acids yield insoluble compounds with the proteïns, which, therefore, also behave as bases: in this respect they exhibit complete analogy to their main decomposition-products, the amino-acids. Among these weak acids are *tannic acid, picric acid. phosphotungstic acid*, and others. The proteïns are completely precipitated from solution by phosphotungstic acid: this method, in addition to coagulation by boiling, and precipitation by alcohol, is employed to separate dissolved proteïns from solution.

236. Various *tests for proteïns* are known, among them the following.

1. *Millon's reagent*, a solution of mercuric nitrate containing nitrous acid, yields a red, coagulated mass on boiling.

2. The *xanthoproteïn-reaction* consists in the formation of a yellow coloration on treatment with warm nitric acid.

3. The *biuret-reaction* depends upon the formation of a fine red to violet coloration when caustic potash is added to a proteïn, and then a two per cent. solution of copper sulphate drop by drop. This reaction derives its name from the fact that biuret, on similar treatment, gives the same coloration (**273**).

Nomenclature.

237. After consultation, the CHEMICAL SOCIETY OF LONDON, the ENGLISH PHYSIOLOGICAL SOCIETY, the AMERICAN PHYSIOLOGICAL SOCIETY, and the AMERICAN SOCIETY OF BIOLOGICAL CHEMISTS have adopted the following system of nomenclature for the proteïns.

1. **Protamines.**—They are the simplest members of the group. Examples are *salmine* and *sturine,* isolated from fish-sperm.

2. **Histones.**—They are more complex than the protamines, but probably each class gradually merges into the other. They are exemplified by the *histones* separated by Kossel from blood-corpuscles. Precipitability by ammonia is one of their distinguishing features.

3. **Albumins.**—*Egg-albumin, serum-albumin,* and *lact-albumin* are typical examples.

4. **Globulins.**—They differ from the albumins in solubility. They are more readily salted out from solution than the albumins. Examples are *serum-albumin, fibrinogen,* and such globulin-derivatives as *fibrin* and *myosin.**

5. **Glutelins.**—Alkali-soluble proteïns of vegetable origin. They are closely related to the globulins.

6. **Gliadins.**—Alcohol-soluble proteïns found in the vegetable kingdom. The principal member of the group is *gliadin,* and Rosenheim has suggested that the class to which it belongs should be designated by its name.

7. **Phospho-proteïns.**—Examples are *vitellin, caseïnogen* (the principal proteïn of milk), and *caseïn* (obtained from caseïnogen by the action of rennet).†

8. **Sclero-proteïns.**‡—This class includes such substances as *gelatin, chondrin, elastin,* and *keratin.* The prefix indicates the

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* The carbohydrate-radical separable in small quantities from many members of Classes 3 and 4 is probably not to be considered as a "prosthetic group"; as it is in the glucoproteïns (9, *c*). The term *myosin* is restricted to the final product formed during *rigor mortis.* Von Fürth's "soluble myogen-fibrin" should be called *soluble myosin.* The two chief proteïns of the muscle-plasma are termed *paramyosinogen* and *myosinogen.*

† The prefix "nucleo-" frequently used in relation to this class is incorrect and misleading. The American Societies include this group with the conjugated proteïns (9). Since the phosphorus-containing radical is not eliminated from the phospho-proteïns like a true prosthetic group, and their cleavage-products contain phosphorus, the English Societies prefer the arrangement indicated.

‡ This term replaces the word "albuminoid" in the limited sense in which most physiologists have employed it, but the American Societies retain the old name.

skeletal origin of its members, and the insolubility of many of them.

9. **Conjugated Proteïns.***—They are substances in which the proteïn molecule is united to a prosthetic group. The principal subdivisions are

a. NUCLEO-PROTEÏNS.—An example is *guanylic acid,* isolated from the pancreas, liver, spleen, and mammary gland.

b. CHROMO-PROTEÏNS.†—*Hæmoglobin* is a type.

c. GLUCO-PROTEÏNS.—They are exemplified by the *mucins.*

10. **Proteïn-derivatives.**‡—They comprise the products of proteïn-hydrolysis, and are classed in four divisions.

a. META-PROTEÏNS.—This group includes the substances formerly classed as "albuminates" or "alkali-albumins," and "syntonins" or "acid-albumins," obtained by the action of an alkali or an acid respectively on albumins and globulins. The name meta-proteïns is preferable because (1) they are derived from globulins as well as albumins, and (2) the termination *ate* implies a salt.

b. PROTEOSES.—They include such substances as *albumose, globulose,* and *gelatose.*

c. PEPTONES.—Further products of hydrolysis which resemble the proteïns in answering the biuret-test, but, unlike them, cannot be salted out from solution.

d. POLYPEPTIDES.—Products of cleavage beyond the peptone stage containing two or more amino-acid-residues. Most of them are synthetical substances, but some of them have been separated

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* The American Societies add "lecitho-proteïns" to this class, but their English *confrères* object on account of the uncertainty as to whether these substances are mechanical mixtures, adsorption-compounds, or true chemical combinations.

† The American Societies employ the term "Hæmoglobins" for chromo-proteïns.

‡ The American Societies include two additional classes in this group: "proteans," insoluble products apparently resulting from the incipient action of water, very dilute acids, or enzymes; and "coagulated proteïns," formed by the action of heat or of alcohol. They are of an ill-defined nature, and the English Societies consider that it is better not to single out for special mention a few of the infinite varieties of insoluble modifications exhibited by proteïns.

from the products of proteïn-hydrolysis. Most of those hitherto prepared do not answer the biuret-test.

238. Particulars of some of the classes named are appended.

The *albumins* are the best known and most readily obtained of the proteïns: all form well-defined crystals, and they are therefore probably among the few proteïns known to be individual chemical compounds; although it has not been proved that these crystals are not mixed crystals containing two or more analogous individuals. They dissolve in water.

Their neutral solutions cannot be salted out with sodium chloride, magnesium sulphate, or a semi-saturated solution of ammonium sulphate—a method of separating them from the globulins, which always occur along with them.

The *globulins* are further distinguished from the albumins by being insoluble in water, although they dissolve in dilute, neutral salt solutions, and in solutions of alkali-metal carbonates. At 30° they can be completely salted out by magnesium sulphate, and partly by sodium chloride. They have not been obtained crystalline.

The *phospho-proteïns* contain phosphorus, and have a distinctly acidic character. All of them turn blue litmus red, and in the free state they are only slightly soluble in water, though their alkali-metal salts and ammonium salts are freely soluble. The solutions of their salts do not coagulate, and can be boiled without undergoing any change.

239. The *sclero-proteïns* differ somewhat in character from the albumins. They occur in the animal economy only in the undissolved state, being the organic constituents of the skeleton and the epidermis. They include various substances, such as *keratin, elastin, gelatin, collagen,* and *chondrin*.

Keratin is the principal constituent of the epidermis, hair, nails, hoofs, and feathers. It is particularly rich in sulphur, of which it contains between four and five per cent. Its decomposition-products resemble those of the albumins. With nitric acid it gives the xanthoproteïn-reaction, the origin of the yellow colour developed when nitric acid comes into contact with the skin.

Elastin is the substance constituting the fibres of connective tissue. Its decomposition-products have the same qualitative composition as those obtained from the albumins. It is insoluble in dilute acids and caustic alkalis.

The *collagens* are the principal sclero-proteïns of the animal body, and the main constituent of connective tissue, such as bone and white fibrous tissue. In several respects they differ from the albumins: they contain 17·9 per cent. of nitrogen; they have not an aromatic nucleus; on hydrolysis, they do not yield tyrosine (391), their chief decomposition-product being glycine, which is accompanied by leucine, aspartic acid, and glutamic acid.

When boiled with water, the collagens are transformed into *gelatin*. This substance is not precipitated from solution by nitric acid or other mineral acids, but it is precipitated by mercuric chloride in presence of hydrochloric acid and by tannic acid.

Chondrin is obtained by extracting cartilage with boiling water, the solution gelatinating as it cools. Acetic acid precipitates chondrin from solution. When boiled with dilute acids, chondrin yields a decomposition-product, *chondrosin*, which reduces FEHLING'S solution. Chondrin is a derivative of gelatin and chondroitinsulphuric acid.

240. In the inferior orders of animal life a series of substances has been discovered approximating more or less closely in chemical properties to the collagens and to elastin. Among them is *spongin*, the principal constituent of sponges, which is much more stable towards caustic soda and baryta-water than collagen. When completely hydrolyzed by boiling with dilute sulphuric acid, it yields leucine and glycine, but no tyrosine, proving it to be a collagen.

On prolonged boiling with water, silk is converted into *fibroïn*, which is not decomposed by water even at 200°, and *sericin*, or *silk-gum*.

Corneïn is the organic constituent of coral. On hydrolysis, it yields leucine and an aromatic substance of unknown composition.

241. Nearly related to the albumins are the *conjugated proteïns*, compounds of proteïns with other substances, usually of a very complex nature. Like the albumins, they are insoluble in alcohol, by which most of them are coagulated.

Nucleo-proteïns derive their name from the fact that they are the principal constituents of the cell-nuclei. They are combinations of proteïns with phosphoric acid or *nucleïc acids* (*Nucleus*, important part of the cells of animals or plants). A nucleïc acid is phosphoric acid which is partially saturated by union with basic substances, such as hypoxanthine, guanine, xanthine, etc. The composition of the nucleo-proteïns differs considerably from that of the albumins: they contain about 41 per cent. of carbon, 31 per cent. of oxygen, and 5·7 per cent. of phosphorus.

The nucleo-proteïns have a markedly acidic character: they are soluble in water and very soluble in caustic alkalis. They answer to the proteïn colour-tests.

Chromo-proteïns are compounds of proteïns with substances containing iron, *hæmoglobin* being the dye of red blood-corpuscles. It decomposes into *globin* and *hæmatin*. In the lungs it unites readily with the oxygen of respired air, yielding *oxyhæmoglobin*. This substance readily gives up its oxygen, and thus the oxidation-processes which maintain the heat of the animal body are carried on. It unites with carbon monoxide to form *carbonyl-hæmoglobin*, which is unable to combine with oxygen: on this reaction depends the poisonous nature of carbon monoxide.

On treatment with acetic acid and sodium chloride, oxyhæmoglobin yields the hydrochloride of hæmatin, called *hæmin*, which crystallizes in characteristic, microscopic plates of a brown-red colour. The reaction furnishes a delicate test for blood.

Gluco-proteïns are compounds of proteïns and carbohydrates. They include the *mucins*, which, like the nucleo-proteïns, are acidic in character. They are insoluble in water, but soluble in a small quantity of lime-water or alkali solution. The liquid thus obtained is neutral, has a glutinous appearance, and is not coagulated by boiling. Unlike the solutions of the albumins, these solutions are not precipitated by nitric acid. When boiled with acids or caustic alkalis, they yield either syntonins or peptones, together with carbohydrates. The presence of the nitrogen-free carbohydrates makes the percentage-amount of nitrogen in the mucins considerably less than in the albumins: its value lies between 11·7 and 12·3 per cent.

Meta-proteïns are mentioned in 235.

Proteoses and peptones can be obtained from all proteïns by suitable hydrolysis. They have the proteïn-character, being insoluble in alcohol, and answering the xanthoproteïn-test and biuret-test (236, 2 and 3). They are produced during digestion by the action of gastric juice on proteïns, and are to be regarded as intermediate products in the hydrolysis of proteïns, the proteoses being nearer the proteïns, and the peptones nearer the amino-acids.

The Structure of the Proteïn Molecule.

242. During last century experimental evidence of the complex structure of the proteïn molecule was accumulated, an important point being the great number of substances formed by the decomposition of albumin. On dry distillation it yields a black oil containing many nitrogen bases; hydrocyanic acid, sulphuretted hydrogen, carbon dioxide, water, benzene, and its homologues, and numerous other bodies being also formed. Both putrefaction and fusion with potassium hydroxide yield ammonia, sulphuretted hydrogen, volatile fatty acids such as butyric acid and valeric acid, amino-acids like leucine and tyrosine, skatole, ptomaïnes, cresol, and other products. By oxidation with various agents it has been possible to isolate hydrocyanic acid, nitriles, benzoïc acid, numerous volatile fatty acids, and other substances.

New products have resulted from each fresh mode of attack, but the analytical methods employed have not shed any light on the structure of the proteïn molecule, since they yield chiefly amorphous and ill-defined substances. The first important step towards the solution of the problem was made by SCHÜTZEMBERGER when he obtained only crystalline derivatives by heating proteïns with bartya-water in an autoclave at 200° for several hours. After removal of the barium, the weight of the decomposition-products formed exceeded that of the initial proteïns, proving that the baryta-water had effected addition of the elements of water, thus hydrolyzing the proteïns to crystalline derivatives.

It was impossible to effect complete separation of the very complex mixture thus obtained, but some of the less soluble constituents, such as leucine and tyrosine, were isolated. The presence in the reaction-product of a number of amino-acids was proved by its properties and the results of analysis. Schutzemberger's brilliant research was rendered more difficult by the necessity of making several hundred analyses. The most important conclusion to be drawn from it is, that the amino-acids constitute the foundation-stones of the proteïns, just as the monoses are the basis of the polyoses (**222**). The fission-products obtained by earlier experimenters were formed by decomposition of the amino-acids.

243. Schützemberger did not succeed in separating the various amino-acids from the mixture obtained by his method of fractional crystallization, but the identification of the various amino-acids derivable from the individual proteïns would be insufficient for a complete comprehension of the structure of the proteïn molecule: the proportion of each acid must also be determined by separation of the complex mixture into its individual constituents. By esterification of the amino-acids (**229**) and fractional distillation *in vacuo* of the mixture of esters, Emil Fischer succeeded not only in isolating the principal constituents, but also in attaining an approximate insight into their relative proportions in the different proteïns. His classical researches have enabled the products of proteïn-hydrolysis to be classified in six divisions.

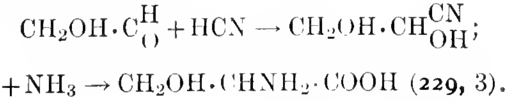
1. **Monobasic monoamino-acids.**—Glycine, alanine, α-aminovaleric acid, leucine (**230**), and phenylalanine,

$$C_6H_5\cdot CH_2\cdot CHNH_2\cdot COOH.$$

2. **Dibasic monoamino-acids.**—Aspartic acid and glutamic acid or aminoglutaric acid.

3. **Diamino-acids.**—Ornithine and lysine (**231**). In the same category may be included arginine, obtained by addition of cyanamide to ornithine (**276**).

4. **Hydroxyamino-acids.**—Tyrosine (**391**) has been known for a long time. Of more recent date is *serine*, $CH_2OH\cdot CHNH_2\cdot COOH$, which is synthesized from glycollaldehyde:



$$CH_2OH\cdot C{}^{H}_{O} + HCN \rightarrow CH_2OH\cdot CH{}^{CN}_{OH};$$

$$+NH_3 \rightarrow CH_2OH\cdot CHNH_2\cdot COOH \ (\mathbf{229},\ 3).$$

This synthesis indicates the constitution of serine, and further confirmation is afforded by its reduction to α-alanine.

To this class also belongs the complicated *diaminotrihydroxydodecanic acid,* $C_{12}H_{26}O_5N_2$, a decomposition-product of caseïn.

5. **Compounds with a closed chain containing nitrogen.**—*α-Tetrahydropyrrolecarboxylic* * *acid* or *proline,* and *hydroxytetrahydropyrrolecarboxylic acid* or *hydroxyproline,* are examples of such derivatives. *Tryptophan* (467), $C_{11}H_{12}O_2N_2$, contains a similar chain: probably skatole (467) which causes the characteristic odour of human fæces, is derived from this fission-product of proteïns. Tryptophan is characterized by the formation of a violet coloration or precipitate on addition of bromine-water. *Histidin,* $C_6H_9O_2N_3$, is probably related to the purine-group (278).

6. **Compounds containing sulphur.**—The only representative of this class is *cystine,* $C_6H_{12}O_4N_2S_2$, which as early as the beginning of last century was identified by WOLLASTON as the principal constituent of certain gall-stones. It has the formula

$$COOH\cdot CHNH_2\cdot CH_2S\text{—}SCH_2\cdot CHNH_2\cdot COOH.$$

On reduction it is converted into *cysteïne,* $COOH\cdot CHNH_2\cdot CH_2SH$, from which atmospheric oxidation regenerates cystine.

The constitution of cystine is proved by its formation from the benzoyl ester of serine (in which the benzoyl-group is attached to nitrogen): fusion with phosphorus pentasulphide converts the CH_2OH-group in this ester into a CH_2SH-group. On elimination of benzoyl, cysteïne is obtained.

EMIL FISCHER has found that the hydrolysis of proteïns can be more readily effected by boiling with concentrated hydrochloric acid, or sulphuric acid of 25 per cent. strength, than by SCHÜTZEMBERGER'S baryta-water method.

244. EMIL FISCHER'S ester-method has rendered possible the approximate quantitative estimation of the products of proteïn-hydrolysis. In the following brief summary of the results obtained it should be noted that usually not more, and often less, than 70 per cent. of the proteïn is recovered in the form of definite compounds, there being a considerable residue which cannot be identified on account of experimental difficulties.

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* *Cf.* foot-note, 460.

On decomposition, some proteïns yield almost exclusively a single amino-acid. Examples of such relatively simple proteïns are *salmine* and *clupeïne*, isolated by Kossel from the testicles of the salmon and herring respectively. On hydrolysis the first yields 84·3 per cent. of arginine, and the second 82·2 per cent.

Usually, however, the proteïns yield a series of amino-acids, the proportions of the individual constituents varying between wide limits. In most proteïns leucine (**230**) is the principal constituent, as in hæmoglobin (**241**), keratin, and elastin (**239**). It is only in fibroïn (**240**) and in gelatin (**239**) that glycine predominates. Of the dibasic amino-acids, aspartic acid (**231**) is generally present in small proportion. Caseïn (**237**, 7) contains a relatively large amount of *glutamic acid.* Tyrosine is the principal decomposition-product of fibroïn: alanine and glycine are formed in smaller proportions. Cystine is an important constituent of keratin: from cow-hair as much as 8 per cent. of it has been obtained, and, on hydrolysis, human hair also yields a large proportion.

The table summarizes the percentage-composition of a few proteïns with respect to certain constituents.

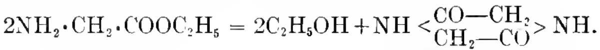
	Hæmo-globin	Caseïn.	Gelatin.	Keratin (from hair)	Fibroïn
Glycine	0	0	16·5	4·7	High
Alanine	4	0·9	0·8		21
Leucine	27·8	10·5	2·1	7·1	1·5
Aspartic acid	4·3	1·2	0·6		
Glutamic acid	1·7	10·7	0·9	3·7	
Arginine	5·2	4·8	7·6		1
Histidine	10·5	2·6	0·4		
Tyrosine	1·3	4·5		3·2	10
Proline	2·3	3·2	5·2	3·4	
Cystine	0·3	0·1		8	

245. Having elucidated the basis of the proteïn molecule, Emil Fischer applied himself to the solution of the greatest problem of organic chemistry—the synthesis of the proteïns. It has long been thought that the amino-acids of the proteïn molecule are linked by their amino-groups, as in *glycylglycine*,

$$NH_2 \cdot CH_2 \cdot CO—NH \cdot CH_2 \cdot COOH,$$

in which the amino-group of one molecule of glycine has become united with the carboxyl-group of another molecule, as in the formation of acid amides. This hypothesis was confirmed by the researches of Emil Fischer. He succeeded, by employing a number of synthetic methods, in uniting various amino-acid-residues, and named the resulting compounds *polypeptides.* They display great analogy to the natural peptones (**237**, 10, *c*). Their synthesis proves that they have the structure indicated.

It is not possible to give here a detailed description of these synthetic methods, but a brief review will not be out of place. On heating, the esters of amino-acids are converted into anhydrides, with elimination of two molecules of alcohol, the reaction sometimes taking place even at ordinary temperatures:

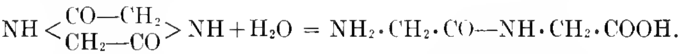


$$2NH_2\cdot CH_2\cdot COOC_2H_5 = 2C_2H_5OH + NH < \begin{matrix} CO—CH_2 \\ CH_2—CO \end{matrix} > NH.$$

Glycine ethyl ester

Diketopiperazine
(Glycine anhydride)

Under the influence of dilute caustic potash, this anhydride takes up one molecule of water, yielding a *dipeptide*, glycylglycine:



$$NH < \begin{matrix} CO—CH_2 \\ CH_2—CO \end{matrix} > NH + H_2O = NH_2\cdot CH_2\cdot CO—NH\cdot CH_2\cdot COOH.$$

Glycylglycine

When a dipeptide is treated with phosphorus pentachloride in acetyl.chloride solution, the carboxyl-group is changed to COCl, and the residue of this acid chloride can be introduced into other amino-acids:

$$NH_2\cdot CH_2\cdot CO—NH\cdot CH_2\cdot COCl + H_2N\cdot CH_2\cdot COOC_2H_5 =$$
$$= NH_2\cdot CH_2\cdot CO—NH\cdot CH_2\cdot CO—NH\cdot CH_2\cdot COOC_2H_5 + HCl.$$

Saponification of this substance yields a *tripeptide*, and so on.

246. The polypeptides, especially from the *tetrapeptides* to the *octapeptides*, are very like the natural peptones, as a short summary of the characteristics of both classes will indicate. Most of them are soluble in water, and insoluble in alcohol: those less soluble are, however, readily dissolved by acids and bases. They usually melt above 200° with decomposition, and have a bitter and insipid taste, and are precipitated by phosphotungstic acid. They answer the biuret-test (236): for the polypeptides the sensitiveness of the reaction augments with increase in the length of the chain. Boiling with concentrated hydrochloric acid for about five hours effects complete hydrolysis. At ordinary temperatures they are stable towards alkalis. They are hydrolyzed by the action of pancreatic juice.

The highest polypeptide prepared by EMIL FISCHER is an *octadecapeptide* containing eighteen amino-acid-residues, fifteen of them being glycine-residues and three being leucine-residues. It has all the characteristics just enumerated, and had it been first discovered in nature, it would certainly have been classed as a proteïn.

This octadecapeptide has the molecular weight 1213: that of most of the fats is much smaller, the figure for tristearin being 891. It is the most complex substance of known structure hitherto obtained by synthesis. The natural proteïns are probably mixtures of various polypeptides for which no mode of separation has been discovered.

The step-by-step decomposition of fibroïn (240) also indicates that the amino-acids in the proteïns have an amino-linking. When it is treated with concentrated hydrochloric acid, *sericoïn* results, and is converted by further boiling with the same acid into a peptone. Pancreatic juice converts this substance into tyrosine (391, 2), and another peptone, which answers the biuret-test. On warming this second peptone with baryta-water, however, it no longer answers this test, and a dipeptide, *glycylalanine,* can be isolated from the products of decomposition.

247. Nothing is known about the molecular weight of the proteïns, except that it must be very great. Attempts to determine it by the cryoscopic method have yielded very small depressions of the freezing-point. It is uncertain whether the observed depressions may have been due to the presence of traces of mineral salts in the albumin employed, since their complete removal is a difficult operation. The negative character of the results might also be due to the presence of the albumin in the colloidal state, since colloids produce only a very small molecular depression ("Inorganic Chemistry," 196).

The proportion of sulphur in the proteïns supports the hypothesis of a high molecular weight. In some varieties it is about 1 per cent. Since there cannot be less than 1 atom, or 32 parts by weight, of sulphur in the proteïn molecule, this percentage points to a molecular weight of 3200, assuming the presence of only one atom of sulphur in the molecule. The percentage of iron in hæmoglobin indicates for this proteïn a molecular weight of about 12,500. Other data give 10,000 as the approximate molecular weight of many proteïns. But there is no gainsaying the fact that these conclusions rest on a very uncertain basis: the close analogy between the higher polypeptides and the natural proteïns makes it probable that the chains of the proteïn molecule do not contain more than about 20 amino-acid-residues.

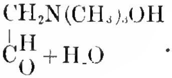
Even if the difference in the nature and in the number of the amino-acids in the proteïn molecule is alone considered, it is evident that an almost infinite variety of proteïns is theoretically possible. Assuming that the proteïn molecule contains 20 different amino-acid-residues, it can be represented by the scheme

$$A_{20}\cdot A_{19}\cdot A_{18}\ldots A_2\cdot A_1,$$

A being an amino-acid-residue. Each fresh grouping of these residues produces a new isomeride. According to the theory of permutations, there are possible $20\times 19\times 18\times\ldots\times 2\times 1$ or approximately $2{\cdot}3\times 10^{18}=2{\cdot}3$ trillion groupings, and hence a like number of isomerides. For other reasons this number must be greatly increased, the first of them being based on stereochemical considerations. Some amino-acids contain asymmetric carbon atoms: if the proteïn molecule contains n of them, the number of stereoisomerides possible is 2^n. Assuming that the value of n in the foregoing example is 10, each of the 2·3 trillion substances could exist in $2^{10}=1024$ optically isomeric forms. The second reason is that the group —CO·NH— can also exist in the tautomeric form (**254**) —C(OH):N—. It is evident that the number of possible isomerides is almost unlimited. It is so great as to make it possible that each of the different kinds of living material has its own individual proteïn; and that the infinite variety of forms found in organic nature is partly the result of isomerism in the proteïn molecule.

AMINO-ALDEHYDES AND AMINO-KETONES.

248. Very few *amino-aldehydes* and *amino-ketones* are known. *Aminoacetaldehyde*, $CH_2NH_2\cdot C^{H}_{O}$, a very unstable compound, can be obtained from *aminoacetal*, $CH_2NH_2\cdot C^{H}_{(OC_2H_5)_2}$, which can be prepared from monochloroacetal, $CH_2\cdot Cl\cdot CH(OC_2H_5)_2$. *Muscarine* is possibly the corresponding trimethylammonium base:



$$\begin{array}{l} CH_2N(CH_3)_3OH \\ | \\ C^{H}_{O} + H_2O \end{array}$$

It is a crystalline, excessively poisonous substance, and is present in certain plants—for example, toad-stool (*Agaricus muscarius*).

Apart from inorganic substances, *chitine* is the principal constituent of the shells of the crustacea, and is best prepared from the shell and claws of the lobster. When boiled with concentrated hydrochloric acid, chitine is almost wholly converted into *glucosamine hydrochloride*, $C_6H_{13}O_5N\cdot HCl$, a well-crystallized salt. Chitine contains an NH_2-group, since like primary amines it evolves nitrogen on treatment with nitrous acid, yielding *chitose*, $C_6H_{12}O_6$, with the properties of an aldose. Thus, it is oxidized by bromine-water to the monobasic *chitonic acid:* further oxidation with nitric acid converts this substance into the dibasic iso*saccharic acid.*

Bromine converts glucosamine hydrochloride into d-*glucosamic acid*, $CH_2OH\cdot(CHOH)_3\cdot CHNH_2\cdot COOH$, which EMIL FISCHER has synthesized by the following method. Ammonia and hydrocyanic acid react with *d*-arabinose to form a compound (**229,** 3),

$$CH_2OH\cdot(CHOH)_3\cdot CHNH_2\cdot CN,$$

and with concentrated hydrochloric acid this yields

$$CH_2OH\cdot(CHOH)_3\cdot CHNH_2\cdot COOH,$$

identical with glucosamic acid. Since this acid is reduced to glucosamine by the method of **207,** 5, the identity of the synthetic amine with the natural product is established.

ALDEHYDO-ACIDS AND KETONIC ACIDS.

Glyoxylic Acid, $\mathrm{COOH\cdot C_{O}^{H}+H_2O}$.

249. *Glyoxylic acid* is the first member of the series of aldehydo-acids. It is present in unripe fruits, and can be prepared by heating dibromoacetic acid, $\mathrm{CHBr_2\cdot COOH}$, with water, or by the electro-reduction of oxalic acid. It also results on the oxidation of alcohol with nitric acid, by the method described under glyoxal (199).

As the above formula shows, glyoxylic acid contains one molecule of water, which cannot be separated from the acid or its salts without their undergoing decomposition. For this reason, the water is often assumed to be in chemical combination (155); thus, $\mathrm{CH(OH)_2\cdot COOH}$, as it is in chloral hydrate (201). In each of these substances the aldehydo-group, $\mathrm{—C_{O}^{H}}$, is under the influence of a strongly negative group; $\mathrm{—CCl_3}$ in chloral, and —COOH in glyoxylic acid. The latter, moreover, possesses all the properties characteristic of aldehydes: it reduces an ammoniacal silver solution, forms an addition-product with sodium hydrogen sulphite, yields an oxime, etc. When boiled with caustic potash, it is converted into glycollic acid and oxalic acid, the formation of which may be explained by the assumption that one molecule of the acid takes up the two hydrogen atoms, and another the oxygen atom, from one molecule of water:

$$\mathrm{2COOH\cdot CHO = COOH\cdot CH_2OH + COOH\cdot COOH.}$$

Pyroracemic Acid, $CH_3 \cdot CO \cdot COOH$.

250. *Pyroracemic (pyruvic) acid*, the first member of the series of ketonic acids, owes its name to its formation by the distillation of either tartaric acid or racemic acid with potassium hydrogen sulphate. It is probable that carbon dioxide is first eliminated from tartaric acid, $COOH \cdot CHOH \cdot CHOH \cdot COOH$, with formation of glyceric acid, $CH_2OH \cdot CHOH \cdot COOH$, which yields pyroracemic acid by loss of one molecule of water; for glyceric acid itself is converted into pyroracemic acid by heating with potassium hydrogen sulphate:

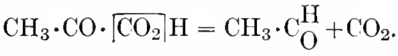
$$CH_2OH \cdot CHOH \cdot COOH - H_2O =$$
$$= CH_2{=}C(OH) \cdot COOH \rightarrow CH_3 \cdot CO \cdot COOH.$$

Pyroracemic acid can be obtained synthetically by hydrolysis of the nitrile formed by the action of potassium cyanide on acetyl chloride:

$$CH_3 \cdot COCl \rightarrow CH_3 \cdot CO \cdot CN \rightarrow CH_3 \cdot CO \cdot CO_2H.$$

This is a general method for the preparation of α-ketonic acids.

When heated to 150° with dilute sulphuric acid, pyroracemic acid yields carbon dioxide and acetaldehyde:



$$CH_3 \cdot CO \cdot \boxed{CO_2}H = CH_3 \cdot C^{H}_{O} + CO_2.$$

At ordinary temperatures pyroracemic acid is liquid, but is solid at low temperatures. It melts at 9°, boils at 165°, and is miscible with water in all proportions: its specific gravity is 1·27 at 20°, and it has an odour resembling that of acetic acid. It is a stronger acid than propionic acid, for which 10^4k is 0·134; for pyroracemic acid 10^4k is 56, which must be explained by assuming the presence of a negative carbonyl-group in juxtaposition to the carboxyl-group.

Pyroracemic acid has all the properties characteristic of ketones: it yields an oxime, a hydrazone, an addition-product with hydrocyanic acid, etc.

The electrolysis of a very concentrated solution of potassium pyroracemate yields acetic acid and diacetyl. The formation of acetic acid may be looked upon as due to the interaction of the anion of the acid and the hydroxyl-ion, after discharge at the anode:

$$CH_3 \cdot CO \cdot COO' + OH' = CH_3 \cdot COOH + CO_2;$$

and that of diacetyl as resulting from the union of two acid anions, with elimination of CO_2:

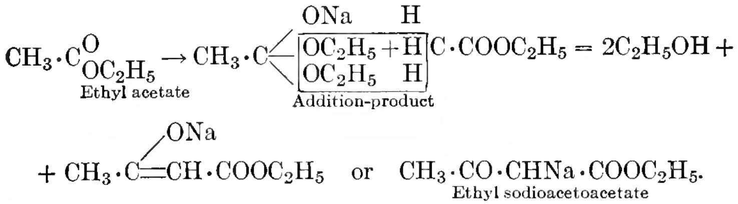
$$\begin{array}{l}CH_3\cdot CO\cdot COO'\\CH_3\cdot CO\cdot COO'\end{array} = CH_3\cdot CO\cdot CO\cdot CH_3+2CO_2.$$

The potassium salts of other ketonic acids are decomposed by electrolysis in an analogous manner.

Acetoacetic Acid, $CH_3\cdot CO\cdot CH_2\cdot COOH$.

251. *Acetoacetic acid* is a β-ketonic acid. It is not of much importance, but its ester, *ethyl acetoacetate*, $CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5$, is an interesting compound.

Ethyl acetoacetate is obtained by CLAISEN's condensation-method (200) through the action of sodium on ethyl acetate in presence of ethyl alcohol:



$$\underset{\text{Ethyl acetate}}{CH_3\cdot C\begin{array}{l}O\\OC_2H_5\end{array}} \rightarrow \underset{\text{Addition-product}}{CH_3\cdot C\begin{array}{l}\quad ONa\qquad H\\ \boxed{\begin{array}{l}OC_2H_5+H\\OC_2H_5\quad\;\; H\end{array}}\end{array}C\cdot COOC_2H_5} = 2C_2H_5OH+$$

$$+\,CH_3\cdot\overset{ONa}{C}{=}CH\cdot COOC_2H_5 \quad\text{or}\quad \underset{\text{Ethyl sodioacetoacetate}}{CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5}.$$

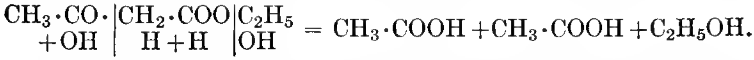
The foregoing explanation of the condensation was proved to be correct in this instance by CLAISEN, who found that ethyl acetoacetate cannot be prepared by the action of sodium on ethyl acetate which has been carefully purified from alcohol. The free ester, $CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5$, can be obtained by treatment of the sodium compound with acetic acid.

Ethyl acetoacetate is a colourless liquid, slightly soluble in water, and characterized by an agreeable odour: it boils at 181°, and has a specific gravity of 1·030 at 15° It can be hydrolyzed in two ways, respectively known as the *ketone decomposition* (*weak hydrolysis*) and the *acid decomposition* (*strong hydrolysis*), on account of the nature of the products.

The ketone decomposition is effected by heating ethyl acetoacetate with dilute sulphuric acid, or with a dilute aqueous solution of alkali, the products being acetone, carbon dioxide, and alcohol:

$$\begin{array}{r|c|l}CH_3\cdot CO\cdot CH_2\cdot & CO_2 & C_2H_5\\ +H & & OH\end{array} = CH_3\cdot CO\cdot CH_3+CO_2+C_2H_5OH.$$

The acid decomposition takes place when ethyl acetoacetate is heated with a very concentrated solution of alcoholic potash or soda:



$$\begin{array}{r|c|l} CH_3\cdot CO\cdot & CH_2\cdot COO & C_2H_5 \\ +OH & H+H & OH \end{array} = CH_3\cdot COOH + CH_3\cdot COOH + C_2H_5OH.$$

The great importance of ethyl acetoacetate for syntheses arises from its capability of undergoing these two decompositions, together with the fact that the Na-atom in ethyl sodioacetoacetate can be substituted by a great variety of groups. If it is replaced by a group R, there is obtained the compound

$$CH_3\cdot CO\cdot CHR\cdot COOC_2H_5,$$

which, by the ketone decomposition, yields a ketone $CH_3\cdot CO\cdot CH_2R$, a reaction affording a general method of synthesizing methylketones (110).

The compound $CH_3\cdot CO\cdot CHR\cdot COOC_2H_5$ can be converted by the acid decomposition into acetic acid, and an acid of the formula $RH_2C\cdot COOH$, which furnishes a general method of preparing monobasic acids synthetically.

Sodium can again react with the compound

$$CH_3\cdot CO\cdot C\overset{*}{H}R\cdot COOC_2H_5,$$

with replacement of the hydrogen atom $\overset{*}{H}$, and production of a compound the Na-atom of which can also be exchanged for the most varied groups, yielding substances of the type

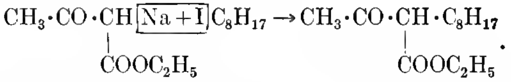
$$CH_3\cdot CO\cdot CRR'\cdot COOC_2H_5.$$

These are converted by the ketone or acid decomposition into

$$CH_3\cdot CO\cdot CHRR' \quad \text{or} \quad CHRR'\cdot COOH.$$

On account of this property, the number of compounds which can be synthesized by the aid of ethyl acetoacetate is very great. The process, called the *acetoacetic-ester synthesis*, is carried out in the way already described for the malonic-ester synthesis (166). A few examples of this synthetical method may be mentioned.

1. *Methylnonylketone*, the principal constituent of oil of rue (from *Ruta graveolens*), can be obtained by the action of *n*-octyl iodide upon ethyl sodioacetoacetate:



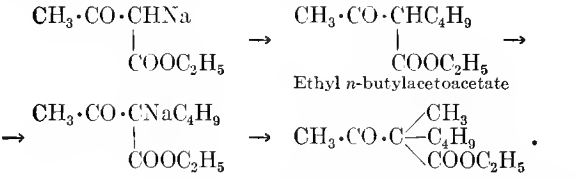
$$\underset{\underset{\displaystyle COOC_2H_5}{|}}{CH_3\cdot CO\cdot CH}\boxed{Na+I}C_8H_{17} \rightarrow \underset{\underset{\displaystyle COOC_2H_5}{|}}{CH_3\cdot CO\cdot CH}\cdot C_8H_{17}.$$

It yields, by the ketone decomposition, methylnonylketone,

$$CH_3\cdot CO\cdot CH_2\cdot C_8H_{17}.$$

Ethyl *n*-octylacetoacetate yields, by the acid decomposition, capric acid, $C_{10}H_{20}O_2$, which must therefore have a normal carbon chain (144).

2. Heptylic acid, which is obtainable from lævulose by the cyanohydrin-synthesis (209, 2), can be synthetically built up from ethyl acetoacetate by the successive introduction of a methyl-group and a *n*-butyl-group: this proves it to be *methyl*-n-*butylacetic acid:*



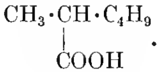
$$\underset{\underset{\displaystyle COOC_2H_5}{|}}{CH_3\cdot CO\cdot CHNa} \rightarrow \underset{\underset{\displaystyle COOC_2H_5}{|}}{CH_3\cdot CO\cdot CHC_4H_9} \rightarrow$$

Ethyl *n*-butylacetoacetate

$$\rightarrow \underset{\underset{\displaystyle COOC_2H_5}{|}}{CH_3\cdot CO\cdot CNaC_4H_9} \rightarrow CH_3\cdot CO\cdot C\begin{cases}CH_3\\ C_4H_9\\ COOC_2H_5\end{cases}.$$

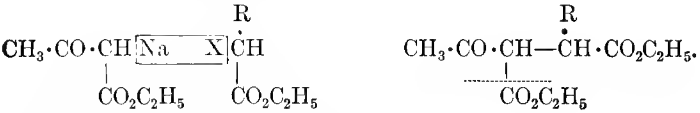
Ethyl methyl-*n*-butylacetoacetate

Ethyl methyl-*n*-butylacetoacetate yields, by the acid decomposition methyl-*n*-butylacetic acid,



$$\underset{\underset{\displaystyle COOH}{|}}{CH_3\cdot CH\cdot C_4H_9}.$$

3. γ-Ketonic acids are obtained by the action of ethyl acetoacetate upon the esters of the α-halogen-substituted fatty acids, followed by the ketone decomposition:

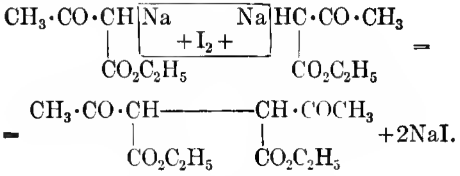


$$\underset{\underset{\displaystyle CO_2C_2H_5}{|}}{CH_3\cdot CO\cdot CH}\boxed{Na\quad X}\overset{R}{\underset{\underset{\displaystyle CO_2C_2H_5}{|}}{CH}} \qquad \underset{\underset{\displaystyle CO_2C_2H_5}{|}}{CH_3\cdot CO\cdot CH}-\overset{R}{CH}\cdot CO_2C_2H_5.$$

This yields, by the ketone decomposition,

$$\underset{\gamma}{CH_3\cdot CO}\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CHR}\cdot CO_2H.$$

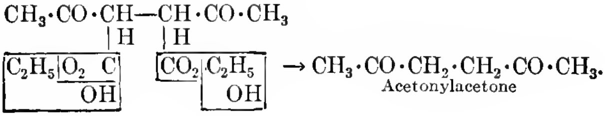
4. When iodine acts upon ethyl sodioacetoacetate, the sodium is removed, and the two residues unite thus:



$$\begin{matrix} CH_3\cdot CO\cdot CH & \boxed{\begin{matrix} Na & & Na \\ & +I_2+ & \end{matrix}} & HC\cdot CO\cdot CH_3 & \\ | & & | & = \\ CO_2C_2H_5 & & CO_2C_2H_5 & \end{matrix}$$

$$= \begin{matrix} CH_3\cdot CO\cdot CH & \text{————} & CH\cdot COCH_3 & \\ | & & | & +2NaI. \\ CO_2C_2H_5 & & CO_2C_2H_5 & \end{matrix}$$

Diethyl diacetylsuccinate is formed, and, when boiled with a 20 per cent. solution of potassium carbonate, loses carbon dioxide and alcohol, with formation of *acetonylacetone* (200):



$$\begin{matrix} CH_3\cdot CO\cdot CH & — & CH\cdot CO\cdot CH_3 \\ |H & & |H \\ \boxed{\begin{matrix} C_2H_5|O_2\ C \\ OH \end{matrix}} & & \boxed{\begin{matrix} CO_2|C_2H_5 \\ OH \end{matrix}} \end{matrix} \rightarrow \underset{\text{Acetonylacetone}}{CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3}.$$

Lævulic Acid, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$.

252. *Lævulic acid* is the simplest γ-ketonic acid: it can be obtained by the synthetical method described in 251, 3—from ethyl acetoacetate by the action of ethyl monochloroacetate; in this instance, in the formula given $R=H$. When hexoses are boiled with concentrated hydrochloric acid, lævulic acid is produced (209, 4): it is usually prepared by this method, which has not yet been fully explained.

Lævulic acid is crystalline: it melts at 33·5°, and boils with slight decomposition at 250°. It yields an oxime and a hydrazone, and an addition-product with hydrocyanic acid: in short, it exhibits all the reactions characteristic of ketones.

Mesoxalic Acid, $C_3H_2O_5+H_2O$.

253. *Mesoxalic acid* is a type of the *dibasic ketonic acids.* Its constitution is proved by the formation of *ethyl mesoxalate* when diethyl dibromomalonate, $Br_2C(COOC_2H_5)_2$, is boiled with baryta-water:

$$(C_2H_5OOC)_2C\boxed{Br_2+Ba}(OH)_2 = (C_2H_5OOC)_2C(OH)_2+BaBr_2.$$

Mesoxalic acid is an important decomposition-product of uric acid. Like glyoxylic acid (249), it can only be obtained with one molecule of water. An ester of the anhydrous acid is, however, known: it very readily adds on water. The constitution $(COOH)_2C(OH)_2$ must therefore be assigned to the free acid (155), which has most of the properties of ketones, just as chloral hydrate (201) and glyoxylic acid show most of the reactions of aldehydes. When boiled with water, mesoxalic acid loses carbon dioxide, forming glyoxylic acid:

$$\boxed{CO_2}H\cdot C(OH)_2\cdot COOH.$$

It is not surprising that a compound containing a carbon atom loaded with four negative groups should break down thus. The decomposition takes place more readily than that of malonic acid, which does not lose carbon dioxide till heated above its melting-point, to 140°–150°.

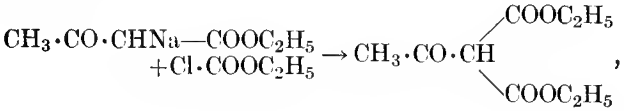
TAUTOMERISM.

254. Ethyl acetoacetate, and in general such substances as 1:3-diketones, which contain the group $—CO—CH_2—CO—$, afford instances of a remarkable kind of isomerism called *tautomerism.* Such compounds behave as though they contained sometimes the group named, sometimes the group $—C(OH):CH—CO—$. A few examples will serve to make this clearer.

When alkyl-groups are introduced into ethyl acetoacetate (251), they become attached to a carbon atom: thus, ethyl methylacetoacetate must have the constitution $CH_3\cdot CO\cdot CH(CH_3)\cdot COOC_2H_5$, since by the ketone decomposition it yields methylethylketone, and by the acid decomposition methylacetic acid, or propionic acid. Since it has this constitution, the formation of methylacetoacetic acid is best explained by supposing that ethyl sodioacetoacetate, $CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5$, is first formed, the Na-atom being then exchanged for a methyl-group by the action of methyl iodide. Most substitutions in ethyl acetoacetate are to be looked upon as taking place thus, with formation of C-derivatives of the ester.

A different effect is produced by the interaction of ethyl sodioacetoacetate and ethyl chlorocarbonate, $Cl\cdot COOC_2H_5$ (269), which results in the formation of two substances in different quantities.

The one formed in smaller quantity results by the reaction indicated above,



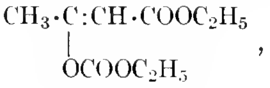
$$\begin{matrix} CH_3\cdot CO\cdot CHNa\text{—}COOC_2H_5 \\ +Cl\cdot COOC_2H_5 \end{matrix} \rightarrow CH_3\cdot CO\cdot CH\begin{matrix} \diagup COOC_2H_5 \\ \\ \diagdown COOC_2H_5 \end{matrix},$$

since this substance is identical with the product obtained by the action of acetyl chloride on diethyl sodiomalonate:

$$CH_3\cdot COCl + NaCH(COOC_2H_5)_2 \rightarrow CH_3CO\cdot CH(COOC_2H_5)_2.$$

It has a *ketonic* structure, since it dissolves in alkalis, indicating that it contains a H-atom replaceable by metals. This must be in the CH-group.

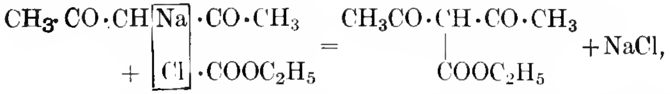
The main product of the reaction, however, is an isomeric compound, which is assumed to have the *enolic* constitution



$$\begin{matrix} CH_3\cdot C:CH\cdot COOC_2H_5 \\ | \\ OCOOC_2H_5 \end{matrix},$$

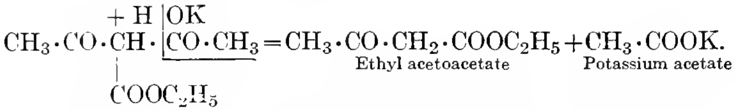
on account of its method of formation and its insolubility in alkalis: this insolubility proves that it does not contain a CH-group between two carboxethyl-groups. The formation of a compound of this type is best explained by the assumption that ethyl sodioacetoacetate has the constitution $CH_3\cdot C(ONa):CH\cdot COOC_2H_5$, as replacement of the Na-atom in this by the group $\text{—}COOC_2H_5$ would lead to the formation of a substance of the above constitution.

An analogous reaction takes place between ethyl chlorocarbonate and sodioacetylacetone: the process is to a small extent in accordance with the equation



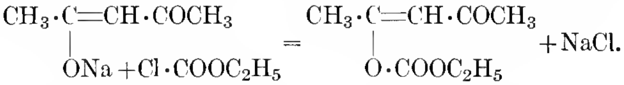
$$\begin{matrix} CH_3\cdot CO\cdot CH\boxed{Na}\cdot CO\cdot CH_3 \\ +\ \boxed{Cl}\cdot COOC_2H_5 \end{matrix} = \begin{matrix} CH_3CO\cdot CH\cdot CO\cdot CH_3 \\ | \\ COOC_2H_5 \end{matrix} + NaCl,$$

since the compound formed is soluble in alkalis, and therefore contains a CH-group in union with three negative groups. When warmed with an equivalent quantity of caustic potash it yields potassium acetate and ethyl acetoacetate:



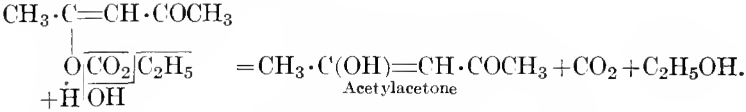
$$\begin{array}{l} \qquad\qquad + H\,|OK \\ CH_3\cdot CO\cdot CH\cdot \underline{|CO\cdot CH_3} = \underset{\text{Ethyl acetoacetate}}{CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5} + \underset{\text{Potassium acetate}}{CH_3\cdot COOK.} \\ \qquad\qquad | \\ \qquad\qquad COOC_2H_5 \end{array}$$

The main reaction, however, is represented by the equation



$$\begin{array}{l} CH_3\cdot C{=}CH\cdot COCH_3 \\ \qquad | \\ \qquad ONa + Cl\cdot COOC_2H_5 \end{array} = \begin{array}{l} CH_3\cdot C{=}CH\cdot COCH_3 \\ \qquad | \\ \qquad O\cdot COOC_2H_5 \end{array} + NaCl.$$

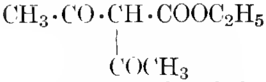
That it takes place thus is proved by the insolubility of the resulting compound in dilute alkalis, which change it, even at ordinary temperatures, into acetylacetone, alcohol, and carbon dioxide:



$$\begin{array}{l} CH_3\cdot C{=}CH\cdot COCH_3 \\ \qquad | \\ \qquad O|\overline{CO_2|}\,\overline{C_2H_5} \\ \quad +H|\overline{OH} \end{array} = \underset{\text{Acetylacetone}}{CH_3\cdot C(OH){=}CH\cdot COCH_3} + CO_2 + C_2H_5OH.$$

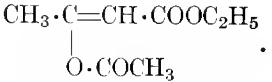
This makes it improbable that the group —$COOC_2H_5$ is in union with a carbon atom.

255. When acid chlorides react with ethyl acetoacetate, it is possible at will to obtain a C-derivative (*ketonic*) or an O-derivative (*enolic*), that is, a compound in which the acid group is linked to the rest of the molecule either through carbon or through oxygen. A C-derivative is obtained by the usual method—the treatment of ethyl sodioacetoacetate with the acid chloride. When, however, ethyl acetoacetate is mixed with pyridine (**449**), and the acid chloride allowed to flow slowly into the mixture, an O-derivative only is formed:



$$\begin{array}{l} CH_3\cdot CO\cdot CH\cdot COOC_2H_5 \\ \qquad\qquad | \\ \qquad\qquad COCH_3 \end{array}$$

C-derivative (soluble in alkali)



$$\begin{array}{l} CH_3\cdot C{=}CH\cdot COOC_2H_5 \\ \qquad | \\ \qquad O\cdot COCH_3 \end{array}.$$

O-derivative (insoluble in alkali)

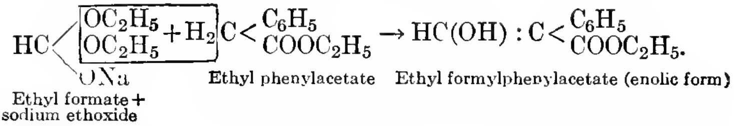
By means of such ambiguous reactions, which characterize many other substances, it is not possible to determine whether a body is a *ketonic compound*, containing the group —$CO\cdot CH_2\cdot CO$—, or an *enolic compound*, with the group —$C(OH){:}CH\cdot CO$—. It was formerly usual to assign one of the two formulæ to substances which exhibited tautomerism, and to explain reactions not in accordance with this formula by assuming that transformation had occurred. It is now known that *a tautomeric substance, in the liquid state or in solution, consists of a mixture of the ketonic compound and the enolic compound*, the proportion of each present being dependent on certain conditions, and this view affords a satisfactory explanation of the observed facts.

The fundamental phenomenon is that tautomerides can react as though they consisted wholly of the ketonic compound, or wholly of the enolic compound. It is explained as follows. If, from a mixture of two isomerides capable of changing into one another with such readiness that the balance between them is rapidly restored, an attempt is made to remove one of the components by chemical methods, the second component should become transformed into the first, on account of the disturbance of the equilibrium: the mixture should then react as though it consisted wholly of the first component. If a chemical reagent which only reacts with the second component is employed, the mixture should behave, for the same reason, as though the latter were the only substance present.

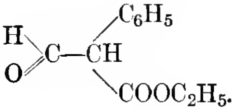
It is, however, possible to effect the separation of tautomerides by chemical means—first, when the disturbed balance is only slowly restored; second, by reactions with nearly the same velocity for both forms, resulting in different products.

These conditions are to a certain extent attained in the reactions described in **254** for ethyl chlorocarbonate. It is by no means certain that the proportion of the isomerides formed is the same as that of the tautomeric forms present in the ethyl acetoacetate, because it is unknown how far the above conditions are fulfilled.

Experience has shown that the enolic form gives an intense colour-reaction with ferric chloride, which is not obtained with the ketonic form. This gives a ready means of identifying a tautomeride, and of recognizing the conversion of one form into the other: it has been applied in various instances, such as the investigation of formylphenylacetic ester. This substance results, by Claisen's condensation-method (**200**) from the action of the ethyl ester of phenylacetic acid upon that of formic acid:


Ethyl formate + sodium ethoxide
Ethyl phenylacetate
Ethyl formylphenylacetate (enolic form)

The ketonic form, or in this instance the "aldo-form," has the formula



The enolic compound is solid, and melts gradually between 60° and 70°: the aldo-compound is a liquid. In dilute alcoholic solution the former gives a deep violet-blue coloration with ferric chloride: the latter gives no coloration. If, however, equally concentrated solutions of the enolic form and the aldo-form are prepared, and an equal quantity of ferric chloride added to each, after some days the solutions are alike, the tint of the enolic compound having become lighter, and the aldo-compound having developed a blue colour. This proves that after standing for some time both solutions contain the aldo-form and the enolic form in equal amounts, since the tint is the same in each solution. It follows that an equilibrium between the opposite transformations exists.

256. Other methods are known by which this transformation of tautomerides can be recognized, of which two may be mentioned. Brühl has shown that rays of light are much more strongly dispersed and refracted by substances containing a double bond than by their isomerides which do not contain such a bond. Since a double bond results from the *enolization* of a ketonic form, it is possible, by a determination of the dispersive and refractive powers, to prove that in alcoholic solution enolic compounds are transformed into ketonic compounds, and *vice versa*.

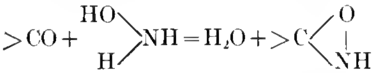
Sir William Perkin discovered another aid to the investigation of these transformations in the electromagnetic rotation of the plane of polarization. The plane of a plane-polarized ray, passed through a tube containing an optically inactive substance, is rotated when an electric current is passed through a wire wound round the tube enclosing the column of liquid. The rotation of the plane of polarization has a definite value for a given compound, supposing that the current, and the length and temperature of the column, are kept constant; and PERKIN found that substances containing a double bond in the molecule occasion a much greater magnetic rotation than isomerides with no such bond.

The conditions upon which the *ketization* of an enolic compound, and the *enolization* of a ketonic compound, respectively depend have been the subject of investigation: the temperature is one of them. CLAISEN found that, at ordinary temperatures, acetyldibenzoylmethane, $CH_3CO \cdot CH(COC_6H_5)_2$ (benzoyl $= C_6H_5CO$, *cf.* **331**), has the ketonic form, its aqueous solution giving no coloration with ferric chloride. When heated to 110°, and quickly cooled to prevent immediate re-transformation, it is found to be converted into the enolic form, since it answers to the colour-test with ferric chloride.

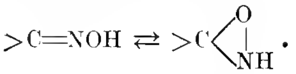
Further, the nature of the solvent has a great influence upon the transformation. In solution in chloroform, an enolic form will remain unchanged for months, while in alcoholic solution it becomes partly or wholly transformed into the ketonic form in the course of a few days.

Tautomerism of Oximes.

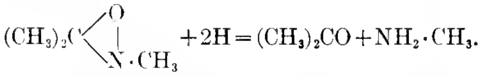
257. The structural formula, $\substack{R \\ R'}{>}C{=}NOH$, has been assigned to the oximes (**112**). The action of hydroxylamine on aldehydes and ketones admits of another explanation, indicated in the scheme:



Experiments directed to proving which of these formulæ is right, have shown that the oximes are tautomeric in the sense of the scheme



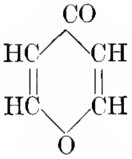
The following exemplifies the method. When acetoxime is treated with methyl iodide, the methyl-group becomes linked to nitrogen, as is proved by reduction of the resulting compound to methylamine and acetone:



But when sodium methoxide is added to a mixture of methyl iodide and the oxime—whereby the sodium derivative of the ketoxime is first formed—there results an isomeric substance convertible by hydrochloric acid into acetone and a compound, $NH_2 \cdot OCH_3$. Heating with hydriodic acid transforms this body into hydroxylamine and methyl iodide, proving that its methyl-group is linked to oxygen.

PYRONE DERIVATIVES.

258. A number of compounds assumed to contain the group

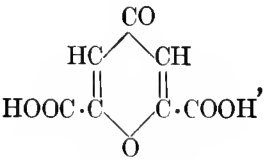


are known: they are called *pyrone derivatives*, and some of them occur naturally.

Chelidonic acid, $C_7H_4O_6$, so called because it is found in *Chelidonium majus* (greater celandine), forms colourless salts, $C_7H_2O_6M_2$: it also yields yellow salts, $C_7H_2O_7M_4$, which are derived from an acid $C_7H_6O_7$, *xanthochelidonic acid*. When set free from its salts, this acid readily loses one molecule of water, and is reconverted into chelidonic acid. By boiling with alkalis, the latter is decomposed almost quantitatively into two molecules of oxalic acid and one molecule of acetone:

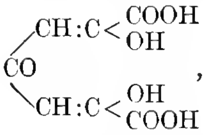
$$C_7H_4O_6 + 3H_2O = \underset{\text{Oxalic acid}}{2C_2H_2O_4} + \underset{\text{Acetone}}{C_3H_6O}.$$

These properties are expressed by the structural formula

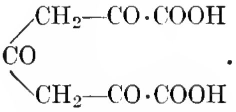


Chelidonic acid

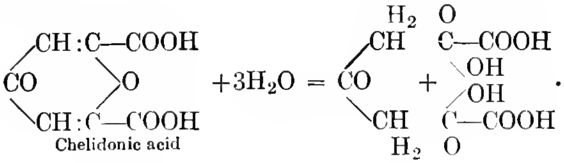
and consequently the acid can be called *pyronedicarboxylic acid.* Xanthochelidonic acid must then have the structural formula



in which the two hydroxyl-hydrogen atoms are also replaceable by metals; or, in its tautomeric form,

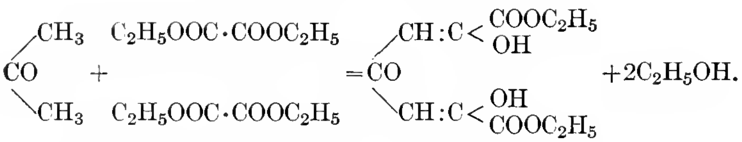


The manner in which it is decomposed by water is evident from the equation



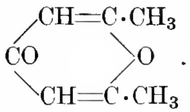
Chelidonic acid

Moreover, a synthesis of chelidonic acid corroborates this formula. The starting-point is acetone, which by CLAISEN's method (200 and 251) can be condensed with two molecules of diethyl oxalate:

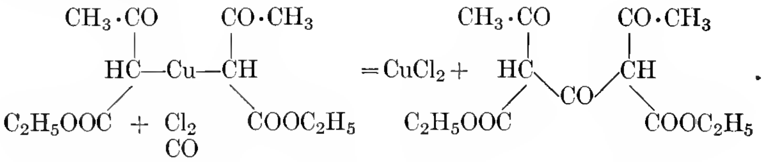


The product is an ester of xanthochelidonic acid. When this is heated with concentrated hydrochloric acid, two objects are simultaneously attained—the ester is saponified, and one molecule of water eliminated. These reactions yield a compound with the structural formula given above for chelidonic acid, and identical with it.

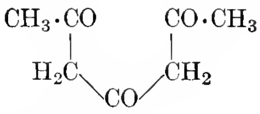
259. An important pyrone derivative is *dimethylpyrone:*



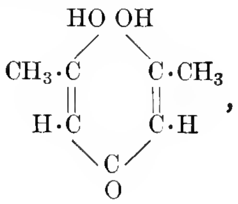
It can be synthesized from ethyl copper-acetoacetate and carbonyl chloride (269):



On saponification with dilute sulphuric acid, two molecules of carbon dioxide are simultaneously eliminated from the molecule, whereupon

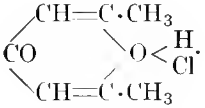


should result. The tautomeride,



however, is formed, and loses one molecule of water, yielding dimethylpyrone.

Dimethylpyrone is characterized by its ability to form addition-products with acids, which must be looked upon as salts. These "salts" are formed by dissolving dimethylpyrone in an aqueous solution of hydrochloric acid, oxalic acid, etc.: they are obtained in a crystalline form by the spontaneous evaporation of the solutions. By dissolving them in a large quantity of water, they are completely hydrolyzed, so that it is improbable that the acid in them is attached to the carbonyl-group. COLLIE and TICKLE, the discoverers of these compounds, accordingly assume the *quadrivalency of the oxygen atom* closing the carbon chain, thus attributing to *dimethylpyrone hydrochloride* the structure



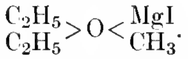
They have named these compounds *oxonium* salts, on account of their analogy to the ammonium salts.

These compounds are proved to be true salts—electrolytes—by various methods. It must be remembered that an aqueous solution of dimethylpyrone has a neutral reaction towards litmus, and that its electric conductivity is very small. Thus, the oxonium base is only feebly basic: if it forms true salts, they must therefore have the properties characteristic of the salts of a weak base. These properties can be summed up in the statement that in aqueous solution such salts are hydrolyzed to a high degree, or, in other words, are to a large extent resolved into free acid and free base ("Inorganic Chemistry," 239). The aqueous solution of a dimethylpyronium salt actually has all the properties characteristic of the solution of a highly hydrolyzed salt. Thus, its solution has a strongly acid reaction: the oxonium salt, however, is partly present as salt in the solution, as WALDEN has demonstrated for *dimethylpyrone picrate*. He found that benzene extracted less picric acid from an aqueous solution of picric acid containing dimethylpyrone than from a solution containing none. This must be explained by assuming the partial formation of a salt, whereby the quantity of free picric acid in the solution is diminished (24).

Hydrolysis can also be detected by observing the depression of the freezing-point. When this is determined for solutions of pure hydrochloric acid of different concentrations, and subsequently after addition of dimethylpyrone to the acid solutions, the depression of the freezing-point in the latter case is less than the sum of the depressions caused by the hydrochloric acid and by the dimethylpyrone in their pure solutions: further, the difference between the value thus calculated and the value observed is the smaller the more the solutions are diluted, as the following example shows. The addition of 3 c.c. of normal hydrochloric acid to 10 c.c. of water caused a depression of 0·846°: the addition of 0·1262 gramme of dimethylpyrone to the mixture caused a depression of 0·936°: the same quantity of dimethylpyrone dissolved in 13 c.c. of water lowered the freezing-point 0·142° The sum of the depressions was thus 0·846° + 0·142° = 0·988°: the difference between this and the observed depression, 0·936°, was therefore 0·052°. When 1 c.c. of normal hydrochloric acid and the same volume (0·1262 gramme) of dimethylpyrone were added to 10 c.c. of water, the difference was only 0·030°, which is in complete agreement with the theory of hydrolytic dissociation. The dissociation increases with the dilution: in fact, a very dilute solution of dimethylpyrone + hydrochloric acid must behave as though the two substances were not in combination at all. Partial combination takes place, however, when the solution is more concentrated, and causes a depression of the freezing-point smaller than the sum of the depressions observed separately for each substance.

260. The power of forming oxonium salts does not seem to be limited to dimethylpyrone and analogous compounds. Von Baeyer and Villiger have shown that oxygen-containing compounds, belonging to various classes of organic bodies, such as alcohols, aldehydes, esters, and other substances, are able to yield crystalline compounds with complex acids, such as hydroferrocyanic acid. It is possible, though not fully established, that these are oxonium salts. They also attempted to obtain trimethyloxonium iodide, $(CH_3)_3O \cdot I$, analogous to the tetra-alkylammonium salts, but were unsuccessful. They are of opinion that Grignard's compounds of alkyl magne-

sium iodides and ether (**82**), such as $CH_3MgI + (C_2H_5)_2O$, must be regarded as oxonium derivatives,



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>O<\!\begin{matrix}MgI\\CH_3\end{matrix}.$$

The power of forming true salts by the addition of acids is especially developed in the alkyl-compounds of the elements of the nitrogen group. Examples also occur among the sulphur compounds: an alkyl sulphide, such as $(C_2H_5)_2S$, can unite with an alkyl iodide to form $(C_2H_5)_3S \cdot I$, trialkylsulphonium iodide, from which the free base can be obtained by the action of moist silver oxide. The extent to which elements of other groups of the periodic system are capable of forming analogous compounds remains to be investigated.

CYANOGEN DERIVATIVES.

Cyanogen, C_2N_2.

261. When mercuric cyanide, $Hg(CN)_2$, is heated, it decomposes into mercury, and a gas, *cyanogen*. A brown, amorphous polymeride, *paracyanogen*, $(CN)_x$, is simultaneously formed: on heating to a high temperature, it is converted into cyanogen. A better method for the preparation of cyanogen is the interaction of solutions of potassium cyanide and copper sulphate; cupric cyanide is formed, and at once decomposes into cuprous cyanide and cyanogen:

$$4KCN + 2CuSO_4 = 2K_2SO_4 + Cu_2(CN)_2 + (CN)_2.$$

The reaction is analogous to that between potassium iodide and a solution of copper sulphate, from which cuprous iodide and free iodine result.

Cyanogen is closely related to oxalic acid. Thus, when ammonium oxalate is heated with a dehydrating agent, such as phosphoric oxide, cyanogen is produced: inversely, when cyanogen is dissolved in hydrochloric acid, it takes up four molecules of water, with formation of ammonium oxalate. These reactions prove cyanogen to be the nitrile of oxalic acid, so that its constitutional formula is $N{\equiv}C{-}C{\equiv}N$.

Cyanogen is also somewhat analogous to the halogens, as its preparation from potassium cyanide and copper sulphate indicates. Moreover, potassium burns in cyanogen as in chlorine, with formation of potassium cyanide, KCN; and when cyanogen is passed into caustic potash, potassium cyanide, KCN, and potassium cyanate, KCNO, are produced, the process being analogous to the formation of potassium chloride, KCl, and potassium hypochlorite, KClO, by the action of chlorine on caustic potash ("Inorganic Chemistry," **56**). Silver cyanide, like silver chloride, is in consistence a cheese-like substance, insoluble in water and dilute acids, and soluble in ammonium hydroxide.

At ordinary temperatures cyanogen is a gas of pungent odour: its boiling-point is $-20 \cdot 7°$. It is excessively poisonous. At high temperatures it is stable, but at ordinary temperatures its aqueous solution decomposes slowly, depositing a brown, amorphous, flocculent precipitate of *azulminic acid*. Cyanogen is inflammable, burning with a peach-blossom coloured flame.

Hydrocyanic Acid, HCN.

262. The salts of *hydrocyanic acid* ("prussic acid") are formed when carbon, nitrogen, and a strong base are in contact at a red heat; for example, when a mixture of carbon and potassium carbonate is strongly heated in a stream of nitrogen. *Cyanides* are also produced when nitrogenous organic substances are heated with an alkali or alkali-metal (**4**). Ammonium cyanide results when ammonia-gas is led over red-hot carbon.

When sparks from an induction-coil are passed through a mixture of acetylene and nitrogen, hydrocyanic acid is formed, and, since acetylene can be obtained by direct synthesis (**133**), this reaction furnishes a method of building up hydrocyanic acid from its elements. Its synthesis is also effected by electrically raising the temperature of a carbon rod to white heat in an atmosphere of hydrogen and nitrogen, 4·7 per cent. of hydrocyanic acid being formed at 2148°. It is usually prepared by heating potassium ferrocyanide (**263**) with dilute sulphuric acid, anhydrous hydrocyanic acid being obtained by fractional distillation of the aqueous distillate. It is a colourless liquid with an odour resembling that of bitter almonds: it boils at 26°, and the solid melts at $-14°$.

When pure, hydrocyanic acid is stable, but its aqueous solution decomposes with formation of brown, amorphous, insoluble substances: the solution contains various compounds, among them ammonium formate.

Like most cyanogen derivatives, hydrocyanic acid is an excessively dangerous poison. The inhalation of hydrogen peroxide, or of air containing chlorine, is employed as an antidote. Like the mercury compounds ("Inorganic Chemistry," 274), its toxic effect depends upon the degree of ionization, so that it must be the cyanogen ions that exert the poisonous action. Other evidence leads to the same conclusion: thus, potassium ferrocyanide, the aqueous solution of which contains no cyanogen ions, is non-poisonous.

Hydrocyanic acid must be looked upon as the nitrile of formic acid: $H \cdot COOH \rightarrow H \cdot CN$. Its formation by the distillation of ammonium formate, and the reverse transformation—referred to above—of hydrocyanic acid into ammonium formate by addition of two molecules of water, favour this view, as does also the formation of hydrocyanic acid when chloroform, $H \cdot CCl_3$, is warmed with alcoholic ammonia and caustic potash (151). Methylamine is obtained by reduction of hydrocyanic acid:

$$H \cdot C \equiv N + 4H = H_3C \cdot NH_2.$$

Hydrocyanic acid is one of the weakest acids, its aqueous solution having low electric conductivity.

Hydrocyanic acid can be obtained from *amygdalin*, $C_{20}H_{27}O_{11}N$, which is a glucoside (215), and is found in bitter almonds and other vegetable-products. In contact with water, amygdalin is decomposed by an enzyme (219), *emulsin*, also present in bitter almonds, into benzaldehyde, hydrocyanic acid, and dextrose:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}O_{11}N} + 2H_2O = \underset{\text{Benzaldehyde}}{C_7H_6O} + HCN + \underset{\text{Dextrose}}{2C_6H_{12}O_6}.$$

Cyanides.

263. The cyanides of the alkali-metals and of the alkaline-earth-metals, and mercuric cyanide, are soluble; other cyanides are insoluble. All have a great tendency to form complex salts, many of which, particularly those containing alkali-metals, are soluble in water and crystallize well. The preparation and properties of some of these salts are described in "Inorganic Chemistry," 308.

Potassium cyanide, KCN, is obtained by heating potassium ferrocyanide, $K_4Fe(CN)_6$, to redness:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

Potassium cyanide is readily soluble in water, and with difficulty in strong alcohol: it can be fused without undergoing decomposition. The aqueous solution is unstable; the potassium cyanide takes up two molecules of water, slowly at ordinary temperatures and quickly on boiling, with elimination of ammonia, and production of potassium formate:

$$KCN + 2H_2O = HCOOK + NH_3.$$

Potassium cyanide always has an odour of hydrocyanic acid, owing to the fact that it is decomposed by the carbon dioxide of the atmosphere into this compound and potassium carbonate.

The aqueous solution of potassium cyanide has a strongly alkaline reaction, the salt being partially hydrolyzed to hydrocyanic acid and caustic potash ("Inorganic Chemistry," **66**). Evidence of this decomposition is also afforded by the possibility of saponifying esters with a solution of potassium cyanide, this furnishing at the same time a method of determining the extent of the hydrolytic decomposition of the salt.

Potassium ferrocyanide, $K_4Fe(CN)_6$, crystallizes in large, sulphur-yellow crystals, with three molecules of water, which can be driven off by the application of gentle heat, leaving a white powder. It is not poisonous (**262**). When warmed with dilute sulphuric acid it yields hydrocyanic acid. On heating with concentrated sulphuric acid, carbon monoxide is evolved; in presence of the sulphuric acid, the hydrocyanic acid first formed takes up two molecules of water, with production of ammonia and formic acid, the latter being immediately decomposed by the concentrated sulphuric acid into carbon monoxide and water (**88**). This method is often employed in the preparation of carbon monoxide.

Cyanic Acid, HCNO.

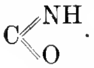
264. *Cyanic acid* is obtained by heating its polymeride, *cyanuric acid* (**267**), and passing the resulting vapours through a freezing-mixture. It is a colourless liquid, stable below 0°. If the flask containing it is removed from the freezing-mixture, so that the temperature rises above 0°, vigorous ebullition takes place, sometimes accompanied by loud reports, and the liquid is converted into a white, amorphous solid. This transformation was first observed by Liebig and Wöhler, by whom the product was called "insoluble cyanuric acid," or *cyamelide*, which is a polymeride of cyanic acid, and probably has the formula $(HCNO)_3$. It has, however, been shown by Senier that the transformation-product contains only about 30 per cent. of cyamelide, the remainder being cyanuric acid: they can be separated by treatment with water, in which cyamelide is very sparingly soluble, much less so than cyanuric acid.

The relationship subsisting between cyanic acid, cyanuric acid, and cyamelide is explained by the following considerations. At ordinary temperatures cyamelide is the stable modification. When cooled below 0°, the vapour of cyanuric acid yields cyanic acid, a transformation analogous to the condensation of phosphorus-vapour at low temperatures to the yellow, and not to the stable red, modification. This is due to the fact that at low temperatures the velocity of transformation of both the unstable forms is very small. Above 0° the velocity of transformation of cyanic acid is much greater, and the polymeric, stable cyamelide is formed, the process, moreover, being considerably accelerated by its own calorific effect. Above 150° cyamelide is converted into the isomeric cyanuric acid. This transformation is analogous to that of rhombic sulphur into monoclinic sulphur, the transition-point being about 150°, although the process is so slow that it could not be determined accurately. A similar slowness prevents observation of the reverse process, the direct transformation of cyanuric acid into cyamelide, so that cyanuric acid remains unchanged for an indefinite period at the ordinary temperature, although it is an unstable modification. In this respect it is comparable with detonating gas ("Inorganic Chemistry," 13).

Above 0° an aqueous solution of cyanic acid changes rapidly into carbon dioxide and ammonia:

$$HCNO + H_2O = H_3N + CO_2.$$

The constitution of cyanic acid itself is unknown, but it yields two series of derivatives which may be regarded as respectively derived from *normal cyanic acid*, $C\lesseqgtr\begin{smallmatrix}OH\\N\end{smallmatrix}$, and from iso*cyanic acid*,



$$C\begin{smallmatrix}\diagup NH\\ \diagdown O\end{smallmatrix}.$$

Cyanogen chloride, CNCl, may be looked upon as the chloride of normal cyanic acid. It is a very poisonous liquid, and boils at 15·5°: it can be obtained by the action of chlorine on hydrocyanic acid, and polymerizes readily to *cyanuric chloride*, $C_3N_3Cl_3$. Cyanogen chloride is converted by the action of caustic potash into potassium chloride and potassium cyanate:

$$CNCl+2KOH = CNOK+KCl+H_2O.$$

Esters of cyanic acid have not been isolated: they are probably formed in the first instance by the action of sodium alkoxides upon cyanogen chloride, since the polymeride, *ethyl cyanurate* $(CNOC_2H_5)_3$, can be readily separated from the reaction-product (**267**).

Esters of iso*cyanic acid*, on the other hand, are well known, and are obtained by the action of alkyl halides on silver cyanate:

$$CO:N\boxed{Ag+I}C_2H_5 = CO\cdot NC_2H_5+AgI.$$

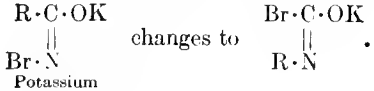
The *iso*cyanic esters are volatile liquids, with a powerful, stifling odour: they, too, polymerize readily, yielding iso*cyanuric esters*, such as $(CONC_2H_5)_3$ (**267**).

The constitution of the *iso*cyanic esters follows from their decomposition into carbon dioxide and an amine, by treatment with water, or better with dilute alkalis:

$$CO:N\cdot CH_3+H_2O = CO_2+NH_2\cdot CH_3.$$

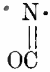
This reaction was first applied by WURTZ to the preparation of primary amines, for obtaining them pure, and free from secondary and tertiary amines.

Primary amines can be obtained from acid amides by the action of bromine and caustic potash (**104**). This is more economically effected by distilling a mixture of the acid amide and bleaching-powder with lime-water. The mechanism of the reaction has been investigated by HOOGEWERFF and VAN DORP. The first product has been isolated; it is a substituted amide, with bromine linked to nitrogen: $R\cdot CO\cdot NH_2 \rightarrow R\cdot CO\cdot NHBr$. The hydrogen of the amino-group can be replaced by metals, owing to the influence of the acid-residue, and this replacement is considerably facilitated by the introduction of a Br-atom. The caustic potash present causes the formation of a compound, $R\cdot CO\cdot NKBr$, which is unstable, but can be isolated. This potassium bromoamide readily undergoes an intramolecular transformation, similar to the BECKMANN transformation (**112**):



$$\begin{array}{c} R\cdot C\cdot OK \\ \| \\ Br\cdot N \end{array} \quad \text{changes to} \quad \begin{array}{c} Br\cdot C\cdot OK \\ \| \\ R\cdot N \end{array}.$$

Potassium bromoamide

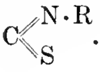
The transformation-product loses KBr, with formation of an *iso*cyanic ester,  $\begin{array}{c}\mathrm{N\cdot R}\\ \|\\ \mathrm{OC}\end{array}$, which is decomposed by the water present into a primary amine and CO_2.

Thiocyanic Acid, HCNS.

265. *Thiocyanic acid* (*sulphocyanic acid*) resembles cyanic acid in its properties, but is much more stable towards water. It can be obtained by treatment of barium thiocyanate with the calculated proportion of dilute sulphuric acid. When the solution is fractionated under diminished pressure, and the vapour passed over calcium chloride to free it from water into a vessel cooled by a freezing-mixture, the anhydrous acid is obtained in the form of a very volatile, pungent-smelling liquid, which changes quickly to a solid polymeride after removal from the freezing-mixture. When warmed with dilute sulphuric acid, thiocyanic acid takes up one molecule of water, and decomposes similarly to cyanic acid (**264**), with production of carbon oxysulphide, COS, instead of CO_2:

$$HCNS + H_2O = H_3N + COS.$$

Potassium thiocyanate is obtained by boiling a solution of potassium cyanide with sulphur. Among other applications it is used in VOLHARD's method of silver-titration. When silver nitrate is added to a solution of potassium thiocyanate, *silver thiocyanate*, AgCNS, is deposited in the form of a white, cheese-like precipitate, insoluble in dilute mineral acids. *Ferric thiocyanate*, $Fe(CNS)_3$, has a dark blood-red colour: its formation is used as a test for ferric salts. The red colour is due to the non-ionized molecules $Fe(CNS)_3$, since neither the ferric ion nor the thiocyanic ion are coloured in solution, and the colour is intensified if ionization is diminished; for example, by the addition of more of the ferric salt or of the thiocyanate. The red colour is removed by agitating the solution with ether, whereas ions cannot be extracted by this means. *Mercury thiocyanate* has the property of intumescing when decomposed by heat ("Pharaoh's serpents").

The constitution of thiocyanic acid, like that of cyanic acid, is unknown, and it resembles the latter in giving rise to two series of esters, the *thiocyanic esters*,  $\mathrm{C}\begin{array}{l}\diagup \mathrm{S\cdot R}\\ \equiv \mathrm{N}\end{array}$, and the iso*thiocyanic esters*,  $\mathrm{C}\begin{array}{l}/\!\!/ \mathrm{N\cdot R}\\ \backslash\!\!\backslash \mathrm{S}\end{array}$.

Thiocyanic esters are obtained by the action of alkyl iodides upon the salts of thiocyanic acid:

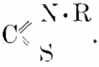
$$\mathrm{CN\cdot S}\boxed{\mathrm{K+I}}\mathrm{C_2H_5} = \mathrm{CN\cdot SC_2H_5+KI}.$$

They are liquids, insoluble in water, and characterized by a leek-like odour. That the alkyl-group in these compounds is in union with sulphur is proved by the nature of the products obtained both by reduction and oxidation. Reduction yields mercaptans and hydrocyanic acid, methylamine being formed from the latter by further reduction:

$$\mathrm{CN\cdot S\cdot C_2H_5+2H = CNH+H\cdot S\cdot C_2H_5}.$$

Alkylsulphonic acids, such as $\mathrm{C_2H_5\cdot SO_2OH}$ (68), are obtained by oxidation.

Under the influence of heat the thiocyanic esters are transformed into *iso*thiocyanic esters: thus, distillation of allyl thiocyanate, $\mathrm{CN\cdot SC_3H_5}$, effects this change.

The *iso*thiocyanic esters are also called *mustard-oils*, after allyl *iso*thiocyanate, to which the odour and taste of mustard-seeds are due. The following reactions prove that these compounds contain an alkyl-group attached to nitrogen, and have the constitution  $\mathrm{C}\langle\begin{matrix}\mathrm{N\cdot R}\\ \mathrm{S}\end{matrix}$. When treated with concentrated sulphuric acid, they take up water, yielding a primary amine and carbon oxysulphide:

$$\mathrm{R\cdot N\!:\!CS+H_2O = R\cdot NH_2+COS}.$$

They are converted by reduction into a primary amine and *trithiomethylene*, $\mathrm{(CH_2S)_3}$, the latter probably resulting from the polymerization of the thiomethylene, $\mathrm{CH_2S}$, first formed, which is unknown in the free state:

$$\mathrm{R\cdot N\!:\!CS+4H = R\cdot NH_2+CH_2S}.$$

Addition-products of the mustard-oils are described in **275** and **276**.

Cyanamide, $\mathrm{CN\cdot NH_2}$, is obtained in various reactions; for instance, by the action of ammonia upon cyanogen chloride. It is a crystalline, hygroscopic solid, and polymerizes readily. Its hydrogen atoms can be replaced by metals; thus, silver yields *silver cyanamide*, $\mathrm{CN\cdot NAg_2}$, which is yellow, and insoluble in dilute ammonium hydroxide, wherein it differs from most silver compounds.

When calcium carbide is heated to redness in a current of nitrogen, *calcium cyanamide* is formed:

$$CaC_2 + N_2 = CN \cdot NCa + C.$$

The absorption of nitrogen is much facilitated by addition of 10 per cent. of calcium chloride: This compound can also be obtained by heating lime and carbon to a red heat in an atmosphere of nitrogen. The crude product is called "Lime-nitrogen" (German, *Kalkstickstoff*), and finds application as an artificial fertilizer, being decomposed slowly by water at ordinary temperatures into ammonia and calcium carbonate;

$$CaCN_2 + 3H_2O = 2NH_3 + CaCO_3.$$

The reaction is much accelerated by heating under pressure. Ammonia can be obtained directly from the nitrogen of the atmosphere by this method.

When barium carbide is heated in nitrogen, it yields barium cyanide:

$$BaC_2 + N_2 = Ba(CN)_2.$$

This reaction affords a means of preparing cyano-derivatives from atmospheric nitrogen.

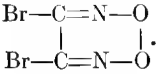
Fulminic Acid.

266. Salts of *fulminic acid* are obtained by the interaction of mercury or silver, nitric acid, and alcohol, in certain proportions. The best known of them is *mercuric fulminate*, $HgC_2O_2N_2$, which is prepared on a large scale, and employed for filling percussion-caps, and for other purposes. Guncotton can be exploded by the detonation of a small quantity of this substance (228); and it produces the same result with other explosives, so that the so-called "fulminating mercury" plays an important part in their application.

Silver fulminate, Ag(CNO), is much more explosive than the mercury salt, and hence is not employed technically. The explosion of these salts has a *brisant* (160), though only local, effect: this enabled Howard, the discoverer of mercuric fulminate, to explode a small quantity in a balloon without injury to the latter, the only effect being to shatter the leaden shells containing the explosive.

Free fulminic acid is a very unstable, volatile substance: it has an odour resembling that of hydrocyanic acid, and is excessively poisonous.

According to NEF, the formula of fulminic acid is $C{=}N\cdot OH$, containing a bivalent carbon atom. When mercuric fulminate is treated with acetyl chloride, a compound of the formula $CH_3\cdot CO(CNO)$ is obtained. In presence of hydrochloric acid the fulminate takes up water, with formation of hydroxylamine and formic acid. It is converted by bromine into a compound, $Br_2C_2O_2N_2$, with the constitutional formula

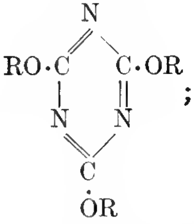


Cyanuric Acid and *iso*Cyanuric Acid.

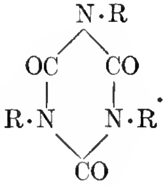
267. *Cyanuric bromide,* $C_3N_3Br_3$, is obtained by heating potassium ferricyanide with bromine at 220°. By heating with water, the bromide is converted into *cyanuric acid,* $(CNOH)_3$. The latter, however, is usually prepared by the action of heat on urea (**273**). Two series of esters are derived from this acid, the *normal* cyanuric and the iso*cyanuric esters,* the former being called "O-esters," and the latter "N-esters."

The normal cyanuric esters are obtained by the action of sodium alkoxides on cyanuric chloride or bromide. The formation of alcohol and cyanuric acid on saponification proves the alkyl-group in these esters to be in union with oxygen. For this reason constitutional formula I. is assigned to them:

I.



II.



The *iso*cyanuric esters result when silver cyanurate is heated with an alkyl iodide. Their alkyl-groups are linked to nitrogen, since, on boiling with alkali, such an ester yields a primary amine and carbon dioxide, a decomposition accounted for in constitutional formula II. The O-esters are formed when an alkyl iodide reacts with silver cyanurate at ordinary temperatures, but their conversion into the N-esters by heating explains the difference in the products obtained at ordinary and at elevated temperatures.

Klason has suggested that cyamelide (**264**) is *iso*cyanuric acid, and that its relation to the *iso*cyanuric esters resembles that of cyanuric acid to the normal cyanuric esters. The formation of cyanuric chloride by the action of phosphorus pentachloride on the normal esters and normal cyanuric acid, and the fact that the *iso*-esters, and, as Senier has shown, cyamelide, do not yield chlorides under this treatment, support this view.

Important evidence in favour of the imino-formula for cyanuric acid has been furnished by Chattaway and Wadmore, who have succeeded in replacing the metal in potassium cyanurate by chlorine. They regard the compound formed as $(O{:}C{:}N{\cdot}Cl)_3$.

DERIVATIVES OF CARBONIC ACID.

268. *Carbonic acid*, H_2CO_3 or $CO(OH)_2$, is not known in the free state, but is supposed to exist in the solution of carbon dioxide in water: it decomposes very readily into its anhydride, carbon dioxide, and water. It is dibasic, and is generally described, with its salts, in inorganic chemistry ("Inorganic Chemistry," **184**). Some of its organic derivatives are dealt with in this chapter.

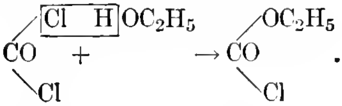
Carbonyl Chloride, $COCl_2$.

269. *Carbonyl chloride* (*phosgene*) is prepared by heating chlorine and carbon monoxide; an equilibrium

$$Cl_2 + CO \rightleftarrows COCl_2,$$

is attained, corresponding at 505° with about 67 per cent. of dissociation. It was called phosgene (φῶς, light; γεννάω, to produce) by J. Davy in 1811, under the impression that its formation by this means can only take place in presence of sunlight, a view since proved to be incorrect. Carbonyl chloride is a gas with a powerful, stifling odour. It dissolves readily in benzene, and the solution is employed in syntheses, both in the laboratory and in the arts.

The reactions of carbonyl chloride indicate that it is the chloride of carbonic acid. It is slowly decomposed by water, yielding hydrochloric acid and carbon dioxide. With alcohol at ordinary temperatures it first forms *ethyl chlorocarbonate:*



$$CO\begin{cases}\boxed{Cl\quad H}OC_2H_5\\ Cl\end{cases} + \quad \rightarrow CO\begin{cases}OC_2H_5\\ Cl\end{cases}.$$

By more prolonged treatment with alcohol, and also by the action of sodium ethoxide, *diethyl carbonate*, $CO(OC_2H_5)_2$, is produced. By the action of ammonia, the two Cl-atoms in carbonyl chloride can be replaced by amino-groups, with formation of the amide of carbonic acid, *urea*, $CO(NH_2)_2$ (272). All these reactions are characteristic of acid chlorides.

The chlorocarbonic esters, also called *chloroformic esters*, are colourless liquids of strong odour, and distil without decomposition. They are employed for the introduction of the group $—COOC_2H_5$ into compounds (254).

The carbonic esters are also liquids, but are characterized by the possession of an ethereal odour: they are insoluble in water, and are very readily saponified.

Carbon Disulphide, CS_2.

270. *Carbon disulphide* is manufactured synthetically by passing sulphur-vapour over red-hot carbon. The crude product has a very disagreeable odour, which can be removed by distilling from fat. The pure product is an almost colourless, highly refractive liquid of ethereal odour. It is insoluble in water, boils at 46°, and has a specific gravity of 1·262 at 20°. Carbon disulphide is poisonous: being highly inflammable, it must be handled with great care. It is an excellent solvent for fats and oils, and finds extensive application in the extraction of these from seeds. It is also employed in the vulcanization of india-rubber.

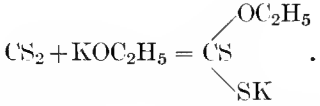
Carbon disulphide is a stable compound, and resists the action of heat, although it is endothermic ("Inorganic Chemistry," 119). It is, however, possible to make its vapour explode by means of mercuric fulminate. The halogens have little action on it at ordinary temperatures; but in presence of a halogen-carrier, chlorine and bromine can effect substitution, with production of carbon tetrachloride and tetrabromide respectively.

Carbon disulphide, like carbon dioxide, is the anhydride of an acid, or an anhydrosulphide. With alkali-metal or alkaline-earth-metal sulphides it yields *trithiocarbonates:*

$$BaS + CS_2 = \underset{\substack{\text{Barium}\\ \text{trithiocarbonate}}}{BaCS_3}.$$

The barium salt is yellow, and dissolves in cold water with difficulty. By the addition of dilute acids to its salts, free *trithiocarbonic acid*, H_2CS_3, can be obtained as an unstable oil. The potassium salt is employed in the destruction of vine-lice.

The potassium salt of *xanthic acid* is formed by the action of potassium ethoxide on carbon disulphide:



$$CS_2+KOC_2H_5=CS\begin{matrix}\diagup OC_2H_5\\ \diagdown SK\end{matrix}.$$

This is effected by agitating carbon disulphide with a solution of caustic potash in absolute alcohol, when *potassium xanthate* separates in the form of yellow, glittering needles. Free xanthic acid is very unstable: it owes its name (ξανθός, yellow) to its cuprous salt, which has a yellow colour, and results from the spontaneous transformation of the brownish-black cupric salt, precipitated from a solution of copper sulphate by the addition of a xanthate.

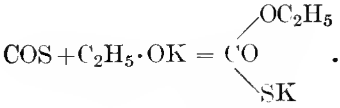
Carbon Oxysulphide, COS.

271. *Carbon oxysulphide* is a colourless, odourless, inflammable gas, and is obtained by the action of sulphuretted hydrogen on *iso*cyanic esters:

$$2CO\cdot NC_2H_5+H_2S=COS+CO(NHC_2H_5)_2.$$

Its formation from *iso*thiocyanic esters is mentioned in **265.** It is also produced when a mixture of carbon monoxide and sulphur-vapour is passed through a tube at a moderate heat.

Carbon oxysulphide is but slowly absorbed by alkalis. It yields salts with metallic alkoxides: these compounds may be regarded as derived from carbonates by simultaneous exchange of oxygen for sulphur:



$$COS+C_2H_5\cdot OK=CO\begin{matrix}\diagup OC_2H_5\\ \diagdown SK\end{matrix}.$$

Urea, $CO<\begin{matrix}NH_2\\NH_2\end{matrix}$.

272. *Urea* owes its name to its occurrence in urine, as the final decomposition-product of the proteïns in the body.

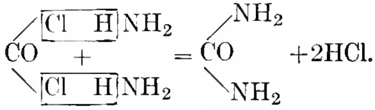
An adult excretes about 1500 grammes of urine, containing approximately 2 per cent. of urea, in twenty-four hours, so that the daily production of this substance amounts to about 30 grammes.

To obtain urea from urine, the latter is first concentrated by evaporation. On addition of nitric acid, *urea nitrate*, $CO(NH_2)_2 \cdot HNO_3$, (**273**) is precipitated, and, on account of impurities, has a yellow colour. The colouring is removed by dissolving the precipitate in water, and oxidizing with potassium permanganate. Urea is set free from the solution of the nitrate by treatment with barium carbonate:

$$\underset{\text{Urea nitrate}}{2CON_2H_4 \cdot HNO_3} + BaCO_3 = 2CON_2H_4 + Ba(NO_3)_2 + H_2O + CO_2.$$

On evaporation to dryness, a mixture of urea and barium nitrate is obtained from which the organic compound can be separated by solution in strong alcohol.

Urea is to be looked on as the amide of carbonic acid, on account of its formation, along with cyanuric acid and cyamelide, from the chloride of this acid, carbonyl chloride, $COCl_2$, this reaction proving its constitution (**269**):

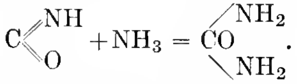


$$CO\begin{matrix}\diagup\boxed{Cl\quad H}NH_2\\ \qquad + \\ \diagdown\boxed{Cl\quad H}NH_2\end{matrix} = CO\begin{matrix}\diagup NH_2\\ \\ \diagdown NH_2\end{matrix} + 2HCl.$$

Carbonyl chloride Urea

A confirmation of this view of the constitution of urea is its formation by the action of ammonia on diethyl carbonate.

Urea is formed by addition of ammonia to *iso*cyanic acid:



$$C\begin{matrix}\diagup NH\\ \diagdown\!\!\diagdown O\end{matrix} + NH_3 = CO\begin{matrix}\diagup NH_2\\ \\ \diagdown NH_2\end{matrix}.$$

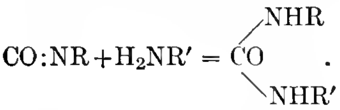
Ammonium *iso*cyanate dissolved in water is transformed into urea on evaporation of the solution. This is the method by which Wöhler effected his classic synthesis of urea, by heating a mixture of potassium cyanate and ammonium sulphate in solution (**1**).

This reaction, which has an important bearing upon the history of organic chemistry, has been studied in detail by James Walker and Hambly. Their researches have shown that the reverse transformation of urea into ammonium *iso*cyanate occurs also, since, on addition of silver nitrate, a solution of pure urea in boiling water yields a precipitate of silver cyanate. An equilibrium is attained:

$$\underset{\text{Urea}}{CO(NH_2)_2} \rightleftarrows \underset{\text{Ammonium } iso\text{cyanate}}{CON \cdot NH_4}.$$

When this equilibrium is reached, the solution only contains a small percentage of *iso*cyanate. It is almost independent of the temperature, proving that the transformation of the systems into one another is accompanied by but slight calorific effect (100).

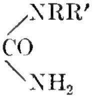
273. *iso*Cyanic esters are decomposed by water, with formation of primary amines and carbon dioxide (264). If the primary amine formed is brought into contact with a second molecule of *iso*cyanic ester, addition takes place, with production of a *symmetrical dialkylurea:*



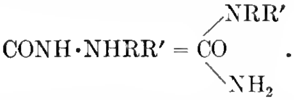
$$CO:NR+H_2NR' = CO\begin{array}{l}\nearrow NHR\\ \searrow NHR'\end{array}.$$

This is a general method for preparing symmetrical dialkylureas.

A *monoalkylurea* is obtained by the action of ammonia, instead of an amine, upon an *iso*cyanic ester.

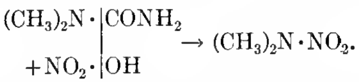


Unsymmetrical dialkylureas, $CO\begin{array}{l}\nearrow NRR'\\ \searrow NH_2\end{array}$, are prepared by the action of *iso*cyanic acid on secondary amines. The method of procedure is analogous to that employed in WÖHLER's synthesis of urea, and consists in warming a solution of the *iso*cyanate of a secondary amine:



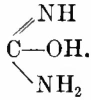
$$CONH\cdot NHRR' = CO\begin{array}{l}\nearrow NRR'\\ \searrow NH_2\end{array}.$$

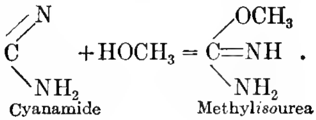
The unsymmetrical dialkylureas are converted by treatment with absolute (100 per cent.) nitric acid into nitro-compounds, which were discovered by FRANCHIMONT, and are called *nitroamines:*



$$\begin{array}{r|l}(CH_3)_2N\cdot & CONH_2\\ +NO_2\cdot & OH\end{array} \rightarrow (CH_3)_2N\cdot NO_2.$$

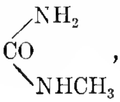
Urea crystallizes in elongated prisms, the crystals resembling those of potassium nitrate: they are very soluble in water, and melt at 132°. Like the amines, urea forms salts by addition of acids, but only one NH_2-group can react thus. Of these salts the *nitrate,* $CON_2H_4\cdot HNO_3$, and the *oxalate,* $2CON_2H_4\cdot C_2H_2O_4$, dissolve with difficulty in solutions of the corresponding acids.

In some of its reactions, notably in certain condensation-processes, urea behaves as though it had the structure  $C\begin{matrix}\nearrow NH\\ -OH\\ \searrow NH_2\end{matrix}$. An ether of this iso*urea* is obtained by addition of methyl alcohol to cyanamide, the reaction being facilitated by the presence of hydrochloric acid:



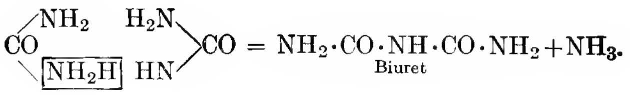
$$\overset{\nearrow N}{\underset{\searrow NH_2}{C}} + HOCH_3 = \overset{\nearrow OCH_3}{\underset{\searrow NH_2}{C}}{=}NH\ .$$

Cyanamide Methyl*iso*urea

This method of formation indicates the constitution of the compound. Another reaction confirming this view is the production of methyl chloride on heating with hydrochloric acid, which points to the fact that the CH_3-group is not in union with nitrogen, since under this treatment *methylurea*,  $\overset{\nearrow NH_2}{\underset{\searrow NHCH_3}{CO}}$, splits off methylamine, $CH_3\cdot NH_2$.

When heated, urea melts; it then begins to evolve a gas, consisting principally of ammonia, but also containing carbon dioxide; after a time the residue solidifies. The following reactions take place.

Two molecules of urea lose one molecule of ammonia, with production of *biuret:*

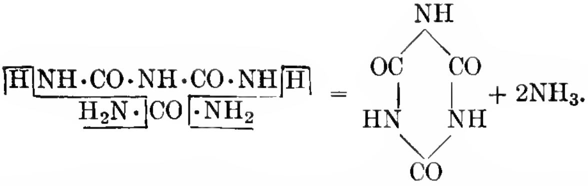


$$CO\begin{matrix}\nearrow NH_2\\ \searrow \boxed{NH_2H}\end{matrix}\quad\begin{matrix}H_2N\searrow\\ HN\nearrow\end{matrix}CO = NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2+NH_3.$$

Biuret

Biuret is a crystalline substance which melts at 190°. When copper sulphate and caustic potash are added to its aqueous solution, it gives a characteristic red to violet coloration ("biuret-reaction").

On further heating, biuret unites with a molecule of unaltered urea, with elimination of ammonia, and formation of cyanuric acid (267):



Hantzsch has shown that the ureïde of cyanuric acid, or *tricyanocarbimido*, $(CN)_3(NH\cdot CO\cdot NH_2)_3$, is formed by heating biuret alone. *Cyanourea* is probably produced first, and then polymerizes:

$$NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2 = H_2O + NH_2\cdot CO\cdot NH\cdot CN \rightarrow (NH_2\cdot CO\cdot NH)_3(CN)_3.$$

Like the acid amides, when heated with bases urea decomposes, yielding carbon dioxide and ammonia.

The quantitative estimation of urea in urine is an operation of considerable importance in physiological chemistry, and is effected by different methods. **Bunsen**'s process depends upon the decomposition of urea into carbon dioxide and ammonia, on heating with an ammoniacal solution of baryta: the carbon dioxide is thus converted into barium carbonate, which can be collected and weighed. In **Knop**'s method the nitrogen is quantitatively liberated by treatment of the urea solution with one of caustic potash and bromine (German, *Bromlauge*), in which potassium hypobromite is present: the percentage of urea can be calculated from the volume of nitrogen liberated. **Liebig**'s titration-method is based upon the formation of a white precipitate of the composition $2CON_2H_4\cdot Hg(NO_3)_2\cdot 3HgO$, when mercuric-nitrate solution is run into a solution of urea of about 2 per cent. concentration. When excess of the mercury salt has been added, a drop of the liquid brought into contact with a solution of sodium carbonate gives a yellow precipitate of basic nitrate of mercury. Urine, however, contains substances which interfere with these methods of estimation: an account of the mode of procedure by which the correct percentage of urea can be ascertained will be found in text-books of physiological chemistry.

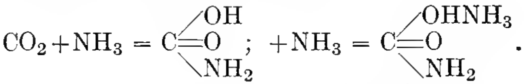
Potassium cyanate and hydrazine hydrate, $H_2N\cdot NH_2 + H_2O$, react together, with formation of *semicarbazide*, $NH_2\cdot CO\cdot NH\cdot NH_2$, a base which melts at 96°, and combines with aldehydes and ketones similarly to hydroxylamine:

$$R_2\cdot C\boxed{O + H_2}N\cdot NH\cdot CO\cdot NH_2 \rightarrow R_2\cdot C{:}N\cdot NH\cdot CO\cdot NH_2.$$

The compounds thus formed are called *semicarbazones;* they sometimes crystallize well, and are employed in the identification and separation of aldehydes and ketones.

Derivatives of Carbamic Acid.

274. *Carbamic acid,* $NH_2 \cdot CO \cdot OH$, which is the semi-amide of carbonic acid, is not known in the free state, but only as salts, esters, and chloride. *Ammonium carbamate* is formed by the union of dry carbon dioxide with dry ammonia:



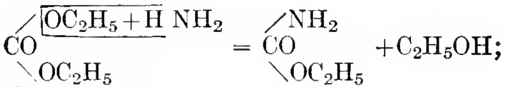
$$CO_2+NH_3 = C\left\langle\begin{matrix} OH \\ =O \\ NH_2 \end{matrix}\right. ; \quad +NH_3 = C\left\langle\begin{matrix} OHNH_3 \\ =O \\ NH_2 \end{matrix}\right. .$$

Ammonium carbamate

When carbon dioxide is passed into an ammoniacal solution of calcium chloride, no precipitate results, since the resulting *calcium carbamate,* $CO\left\langle\begin{matrix} Oca^* \\ NH_2 \end{matrix}\right.$, is soluble in water.

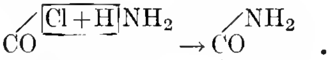
When the salts of carbamic acid are heated in solution, they readily take up water, forming carbonates.

The esters of carbamic acid are called *urethanes.* They are formed by the action of ammonia or amines upon the esters of carbonic acid or chlorocarbonic acid:



$$CO\left\langle\begin{matrix} \boxed{OC_2H_5+H}\ NH_2 \\ OC_2H_5 \end{matrix}\right. = CO\left\langle\begin{matrix} NH_2 \\ OC_2H_5 \end{matrix}\right. +C_2H_5OH;$$

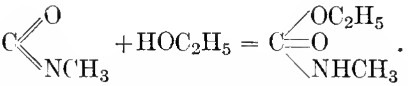
Diethyl carbonate Urethane



$$CO\left\langle\begin{matrix} \boxed{Cl+H}NH_2 \\ OC_2H_5 \end{matrix}\right. \rightarrow CO\left\langle\begin{matrix} NH_2 \\ OC_2H_5 \end{matrix}\right. .$$

Ethyl chlorocarbonate

Urethanes also result in the action of alcohol upon *iso*cyanic esters:



$$C\left\langle\begin{matrix} O \\ NCH_3 \end{matrix}\right. +HOC_2H_5 = C\left\langle\begin{matrix} OC_2H_5 \\ =O \\ NHCH_3 \end{matrix}\right. .$$

Urethanes are also obtained by boiling acid azides(105) with alcohol:

$$R.CON_3+C_2H_5OH = R\cdot NHCOOC_2H_5+N_2$$

---

* $ca = \frac{1}{2}Ca$.

Since the azides are easily prepared from the corresponding acids, and the urethanes readily yield the corresponding amines, the carboxyl-group can be replaced by the amino-group:

$$\underset{\text{Acid}}{R\cdot COOH} \rightarrow \underset{\text{Ester}}{R\cdot COOC_2H_5} \rightarrow \underset{\text{Hydrazide}}{R\cdot CONHNH_2} \rightarrow \underset{\text{Azide}}{R\cdot CON_3} \rightarrow$$

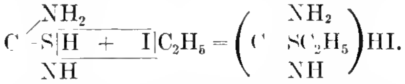
$$\rightarrow \underset{\text{Urethane}}{R\cdot NHCOOC_2H_5} \rightarrow \underset{\substack{\text{Primary}\\\text{amine}}}{R\cdot NH_2}.$$

Urethanes distil without decomposition: ordinary urethane, $CO\begin{smallmatrix}\diagup OC_2H_5\\ \diagdown NH_2\end{smallmatrix}$, melts at 51°, and is very readily soluble in water. When boiled with bases, it decomposes into alcohol, carbon dioxide, and ammonia. Concentrated nitric acid converts it into *nitrourethane*, $C_2H_5O\cdot CO\cdot NH\cdot NO_2$; and on careful hydrolysis this substance yields *nitroamine*, $NH_2\cdot NO_2$.

Thiourea, $CS(NH_2)_2$.

275. Ammonium *iso*thiocyanate yields *thiourea* in a manner analogous to the formation of urea from ammonium *iso*cyanate (272). The transformation of the thio-compound can in this instance be effected by heating it in the dry state, but is no more complete than that of ammonium cyanate, since thiourea is converted by heat into ammonium *iso*thiocyanate. Alkyl-derivatives of thiourea result from addition of ammonia or amines to the mustard-oils (265), the reaction being similar to the formation of alkyl-substituted ureas from *iso*cyanic esters (273).

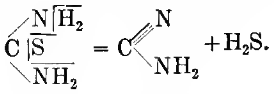
These modes of formation prove that the constitution of thiourea is expressed by the formula $CS(NH_2)_2$, being similar to that of urea. Derivatives of thiourea are known, however, which point to the existence of a tautomeric form $C\begin{smallmatrix}\diagup NH_2\\ -SH\\ \diagdown NH\end{smallmatrix}$ (273): thus, on addition of an alkyl iodide, compounds are obtained in accordance with the equation



$$C\begin{matrix}\diagup NH_2\\ -S\,|\,H\\ \diagdown NH\end{matrix} + I\,|\,C_2H_5 = \left(C\begin{matrix}\diagup NH_2\\ -SC_2H_5\\ \diagdown NH\end{matrix}\right)HI.$$

The alkyl-group in this compound is linked to sulphur; for it decomposes with formation of mercaptan, and on oxidation yields a sulphonic acid.

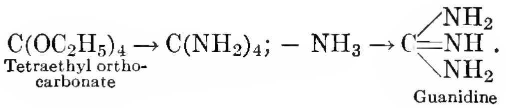
Thiourea forms well-defined crystals, melting at 172°, and readily soluble in water, but with difficulty in alcohol. On treatment with mercuric oxide, it loses sulphuretted hydrogen, forming cyanamide:



$$C\begin{matrix}/N\boxed{H_2}\\ \boxed{S}\\ \backslash \overline{NH_2}\end{matrix} = C\begin{matrix}\equiv N\\ \backslash NH_2\end{matrix} + H_2S.$$

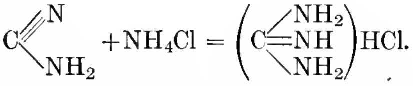
Guanidine, CH_5N_3.

276. *Guanidine* is formed by the interaction of ammonia and orthocarbonic esters or chloropicrin, CCl_3NO_2. This probably results from addition of four amino-groups to the carbon atom, the compound formed then losing one molecule of ammonia:



$$\underset{\text{Tetraethyl ortho-carbonate}}{C(OC_2H_5)_4} \rightarrow C(NH_2)_4; \ - NH_3 \rightarrow \underset{\text{Guanidine}}{C\begin{matrix}/NH_2\\ =NH\\ \backslash NH_2\end{matrix}}.$$

This method of preparing guanidine establishes the constitutional formula indicated. Further evidence is afforded by its synthesis by heating cyanamide with an alcoholic solution of ammonium chloride:



$$C\begin{matrix}\equiv N\\ \backslash NH_2\end{matrix} + NH_4Cl = \left(C\begin{matrix}/NH_2\\ =NH\\ \backslash NH_2\end{matrix}\right)HCl.$$

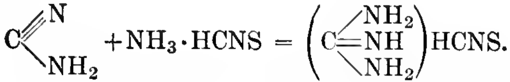
Guanidine is generally prepared by heating ammonium thiocyanate for six hours at temperatures rising from 180° to 205°, air being blown through the melt to oxidize the evolved sulphuretted hydrogen to sulphur and water, and thus obviate the formation of secondary products:

$$2S:C:NH \cdot NH_3 = H_2S + (CH_5N_3)HCNS.$$

It is obtained in the form of *guanidine thiocyanate*, the reaction taking place in the following stages:

$$\underset{\text{Ammonium thiocyanate}}{SCNH \cdot NH_3} \rightarrow \underset{\text{Thiourea}}{CS(NH_2)_2} \rightarrow \underset{\text{Cyanamide}}{H_2N \cdot CN}.$$

The cyanamide unites with a molecule of the unaltered ammonium thiocyanate:



$$C\begin{smallmatrix}\diagup\!\!\!\!\equiv N\\ \\ \diagdown NH_2\end{smallmatrix} + NH_3\cdot HCNS = \left(C\begin{smallmatrix}\diagup NH_2\\ = NH\\ \diagdown NH_2\end{smallmatrix}\right)HCNS.$$

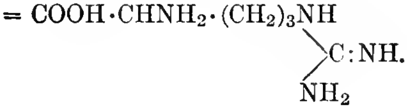
Guanidine thiocyanate

Guanidine is a colourless, crystalline substance, and readily absorbs moisture and carbon dioxide from the atmosphere. It is a strong base, unlike urea, which has a neutral reaction: the strengthening of the basic character, occasioned by exchange of carbonyl-oxygen for an imino-group, is worthy of notice. Guanidine yields many well-defined, crystalline salts.

Nitroguanidine, $C\begin{smallmatrix}\diagup NH\cdot NO_2\\ = NH\\ \diagdown NH_2\end{smallmatrix}$, is obtained in solution by the action of fuming nitric acid upon guanidine: dilution with water precipitates the nitroguanidine, which is very slightly soluble in water. On reduction, it yields *aminoguanidine*, $C\begin{smallmatrix}\diagup NH\cdot NH_2\\ = NH\\ \diagdown NH_2\end{smallmatrix}$, which, on boiling with dilute acids or alkalis, decomposes with formation of carbon dioxide, ammonia, and diamide or hydrazine, $H_2N\cdot NH_2$ ("Inorganic Chemistry," 114). This reaction proves the constitution of nitroguanidine and aminoguanidine.

An important derivative of guanidine is *arginine*, $C_6H_{14}O_2N_4$, obtained from proteïns. It can be synthesized by the action of cyanamide on ornithine (231):

$$\underset{\text{Ornithine}}{COOH\cdot CH(NH_2)\cdot(CH_2)_3\cdot NH_2} + \underset{\text{Cyanamide}}{CN_2H_2} =$$



$$= COOH\cdot CHNH_2\cdot(CH_2)_3\begin{smallmatrix}NH\diagdown\\ \\ NH_2\diagup\end{smallmatrix}C:NH.$$

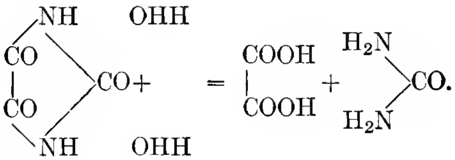
Arginine

It is doubtful whether the cyanamide is added at the δ-NH_2-group, as represented in the equation, or at the α-NH_2-group.

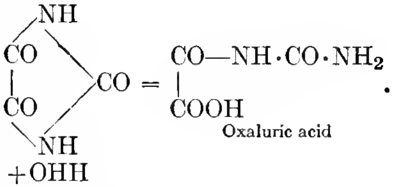
URIC-ACID GROUP.

277. *Uric acid,* $C_5H_4O_3N_4$, derives its name from its presence in small amount in urine: it is the nucleus of an important group of urea derivatives. It is closely related to the *ureïdo-acids* and the *acid-ureïdes* (*ureïdes*), which are amino-acids and acid amides, containing the urea-residue, $NH_2 \cdot CO \cdot NH—$, instead of the NH_2-group.

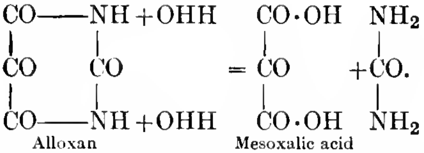
Parabanic acid, $C_3H_2O_3N_2$, is an acid-ureïde: it is obtained by the oxidation of uric acid. When warmed with alkalis for a long time, parabanic acid takes up two molecules of water, forming urea and oxalic acid, a reaction which proves it to be *oxalylurea:*


Parabanic acid (Oxalylurea)

On careful treatment with alkalis, it takes up only one molecule of water, yielding *oxaluric acid:*


Oxaluric acid

Alloxan, $C_4H_2O_4N_2$, is an important decomposition-product of uric acid, from which it is obtained by oxidation with nitric acid: it can also be prepared by other methods. It is *mesoxalylurea,* since, on treatment with alkalis, it takes up two molecules of water, with production of urea and mesoxalic acid:



Carbon dioxide and parabanic acid are produced by the oxidation of alloxan with nitric acid.

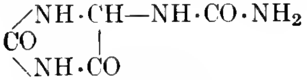
Alloxan is converted by reduction into *alloxantine* :

$$2C_4H_2O_4N_2 + 2H = C_8H_6O_8N_4.$$

Alloxantine

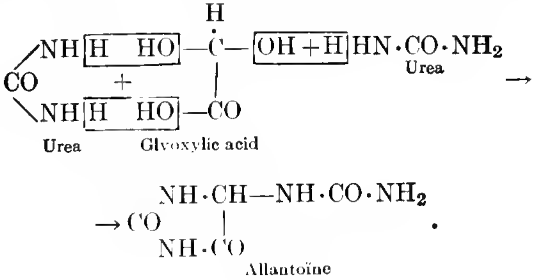
Alloxantine is also formed directly from uric acid by evaporating it to dryness with dilute nitric acid. When treated with ammonia, it forms a purple-red dye, *murexide*, $C_8H_8O_6N_5$. The formation of murexide is employed as a test for uric acid. Alloxantine dissolves with difficulty in cold water, and gives a blue colour with baryta-water. There is still doubt as to the constitution of these compounds.

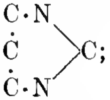
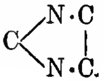
Allantoïne, $C_4H_6O_3N_2$, is formed in the oxidation of uric acid with potassium permanganate, a fact which has an important bearing on the constitution of this acid. Allantoïne has the structure

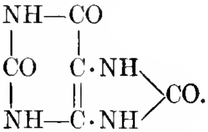


Allantoïne

since it can be obtained synthetically by heating glyoxylic acid with urea:



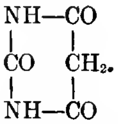
The formation of alloxan and allantoïne from uric acid gives an insight into its constitution, the production of the first indicating the presence of the complex ; and of the second, the presence of two urea-residues, together with the complex . These are accounted for in the structural formula



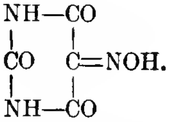
Uric acid

This formula also gives full expression to the other chemical properties of uric acid.

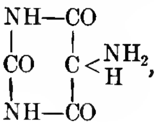
The following synthesis affords confirmation of the accuracy of the constitution indicated. Malonic acid and urea combine to form *malonylurea* or *barbituric acid :*



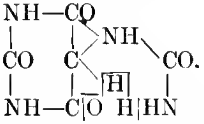
On treatment with nitrous acid, this substance yields an *iso*nitroso-compound which can also be obtained from alloxan and hydroxylamine, *violuric acid :*



On reduction, violuric acid gives *aminobarbituric acid :*



which, like the amines, adds on one molecule of *iso*cyanic acid on contact with potassium cyanate, forming

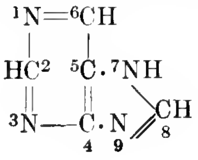


This substance is pseudo*uric acid*, and differs from uric acid only in containing the elements of another molecule of water. Boiling with a large excess of 20 per cent. hydrochloric acid eliminates this molecule of water as indicated in the formula, the treatment yielding a substance with the constitution assigned to uric acid, and identical with this compound.

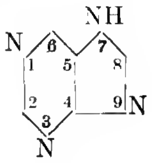
Uric acid dissolves with difficulty in water, but is soluble in concentrated sulphuric acid, from which it is precipitated by addition of water. It forms two series of salts, by exchange of one or two hydrogen atoms respectively for metals. *Normal sodium urate*, $C_5H_2O_3N_4Na_2 + H_2O$, is much more soluble in water than *sodium hydrogen urate*, $2C_5H_3O_3N_4Na + H_2O$. *Normal lithium urate* is moderately soluble in water.

Uric acid is present in urine, and is the principal constituent of the excrement of birds, reptiles, and serpents: it can be conveniently prepared from serpent-excrement. In certain pathological diseases of the human organism, such as gout, uric acid is deposited in the joints in the form of sparingly soluble primary salts. On account of the solubility of lithium urate, lithia-water is prescribed as a remedy.

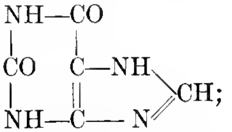
278. A number of compounds with the same carbon-nucleus as uric acid occur in nature, partly in the animal, and partly in the vegetable, kingdom. To the former belong *hypoxanthine*, $C_5H_4ON_4$; *xanthine*, $C_5H_4O_2N_4$; and *guanine*, $C_5H_5ON_5$: to the latter belong the vegetable bases *theobromine*, $C_7H_8O_2N_4$; and *caffeïne*, $C_8H_{10}O_2N_4$. To assign a rational nomenclature to these substances and other members of the same group, Emil Fischer regards them as derivatives of *purine* (**279**), the C-atoms and N-atoms of which are numbered as indicated in the formula



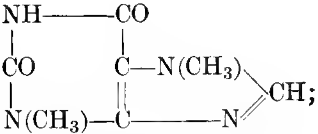
or



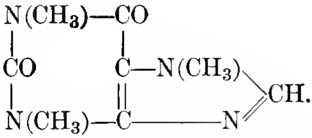
Xanthine, theobromine, and caffeïne have the following structural formulæ and rational names:



Xanthine or 2:6-dioxypurine



Dimethylxanthine, theobromine, or 3:7-dimethyl-2:6-dioxypurine



Trimethylxanthine, caffeïne, theïne, or 1:3:7-trimethyl-2:6-dioxypurine

Theobromine and caffeïne result from the introduction of methyl-groups into xanthine.

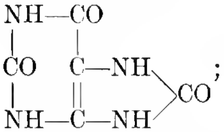
Xanthine, $C_5H_4O_2N_4$, is present in all the tissues of the human body. It is a colourless powder, soluble with difficulty in water, and possessing a weak basic character. On oxidation, it yields alloxan and urea.

Theobromine, $C_7H_8O_2N_4$, exists in cocoa, and is prepared from this product. It is only slightly soluble in water, and is converted by oxidation into *monomethylalloxan* and *monomethylurea*.

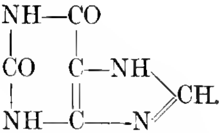
Caffeïne or *theïne*, $C_8H_{10}O_2N_4$, is a constituent of coffee and tea It crystallizes with one molecule of water in long, silky needles, and is moderately soluble in water. It is generally prepared from tea-dust. On careful oxidation it yields *dimethylalloxan* and *monomethylurea*.

The position of the methyl-groups in theobromine and caffeïne is proved by the formation of these oxidation-products.

There is an evident resemblance between the constitution of uric acid and that of xanthine:



Uric acid

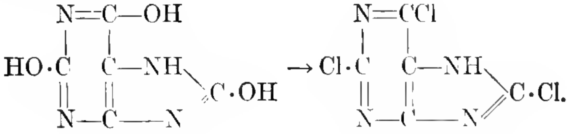


Xanthine

These formulæ indicate the possibility of obtaining xanthine by the reduction of uric acid, and up to the year 1897 numerous unsuccessful attempts were made to prepare it by this method, a reaction ultimately effected by Emil Fischer in that year. He has discovered several methods of converting uric acid into xanthine and its methyl-derivatives mentioned, including one by which the manufacture of the therapeutically important bases, theobromine and caffeïne, seems to be possible.

279. Direct replacement of oxygen in uric acid by hydrogen does not seem possible. Emil Fischer has, however, substituted chlorine for oxygen by means of phosphorus oxychloride. Various methods of replacing the chlorine atoms in these halogen derivatives by other groups or atoms have been devised.

When uric acid is treated with phosphorus oxychloride, the first product is 8-*oxy*-2:6-*dichloropurine:* on further careful treatment with the same reagent, this substance is converted into 2:6:8-*trichloropurine:*



Tautomeric form of uric acid

2:6:8-Trichloropurine

The behaviour of uric acid in this reaction accords with the tautomeric (**254**) formula of trihydroxypurine, the phosphorus oxychloride replacing the hydroxyl-groups with chlorine atoms in a normal manner.

At 0°, and in presence of hydriodic acid and phosphonium iodide, trichloropurine changes into *di-iodopurine:*

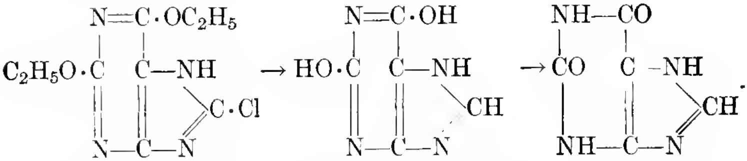
$$C_5HN_4Cl_3 + 4HI = C_5H_2N_4I_2 + 3HCl + 2I$$

Reduction of the aqueous solution of di-iodopurine with zinc-dust yields *purine*, a white crystalline substance, melting at 216°-217°, and very readily soluble in water. It is a weak base, since it does not turn red litmus blue.

Xanthine is thus obtained from trichloropurine.

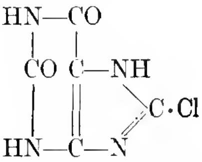
Cl-atom 8 in this compound is very stable towards alkalis, whereas Cl-atoms 2 and 6 are displaced with comparative ease: when trichloropurine is treated with sodium ethoxide, Cl-atoms

2 and 6 are exchanged for ethoxyl-groups. On heating the compound thus obtained with a solution of hydriodic acid, the ethyl-groups are replaced by hydrogen, Cl-atom 8 being simultaneously exchanged for a H-atom, with formation of xanthine:



2:6-Diethoxy-8-chloropurine Xanthine (tautomeric form) Xanthine

When 2:6-*diethoxy-8-chloropurine* is heated with hydrochloric acid, only the ethyl-groups are replaced by hydrogen, with production of a compound of the formula



,

the tautomeric enolic form changing to the ketonic modification. On methylating this substance, its three H-atoms are exchanged for methyl-groups, yielding *chlorocaffeïne*, which can be converted by nascent hydrogen into caffeïne. This process, therefore, affords a means of preparing caffeïne from uric acid.

Emil Fischer has discovered a very characteristic and simple mode of effecting this methylation—agitating an alkaline, aqueous solution of uric acid with methyl iodide, whereby the four hydrogen atoms are replaced by methyl-groups, with formation of a *tetramethyluric acid*. On treating this with phosphorus oxychloride $POCl_3$, chlorocaffeïne is formed:

$$3C_5O_3N_4(CH_3)_4+POCl_3 = 3C_5O_2N_4(CH_3)_3Cl+PO(OCH_3)_3.$$

It can be converted by nascent hydrogen into caffeïne.

Electro-reduction of Purine Derivatives.

280. Tafel has stated that caffeïne, xanthine, uric acid, and similar compounds reducible with difficulty by the ordinary methods readily take up hydrogen evolved by electrolysis. For this purpose the compounds are dissolved in sulphuric acid, the strength of which is varied to suit the particular compound, and lies between 50 and 75 per cent. This solution is contained in a porous cell, and has a lead cathode immersed in it. This cell is placed in sulphuric acid of 20 to 60 per cent. strength, which contains the anode. The hydrogen evolved at the cathode by the current readily effects the reduction of these compounds.

Xanthine and its homologues take up four atoms of hydrogen, becoming transformed into *deoxy-derivatives:*

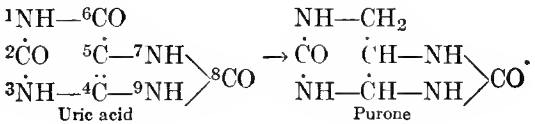
$$\underset{\text{Caffeïne}}{C_8H_{10}O_2N_4}+4H = \underset{\text{Deoxycaffeïne}}{C_8H_{12}ON_4}+H_2O.$$

The deoxy-compounds are stronger bases than their parent-substances, which have very weakly basic properties.

The reduction of uric acid requires six hydrogen atoms, and yields *purone:*

$$\underset{\text{Uric acid}}{C_5H_4O_3N_4}+6H = \underset{\text{Purone}}{C_5H_8O_2N_4}+H_2O.$$

The oxygen atom of carbon atom 6 is replaced by hydrogen. Two hydrogen atoms are simultaneously added at the double bond of the uric-acid molecule:



Uric acid   Purone

This structure is proved by the fact that on heating with baryta-water purone yields two molecules of carbon dioxide: it must, therefore, contain two unaltered urea-residues, which necessitates the presence of carbonyl-groups 2 and 8. It can be proved that carbonyl-group 6 is also the group reduced in xanthine and its homologues.

Purone is neither a base nor an acid, and is not attacked by oxidizing agents. When warmed with a 10 per cent. solution of caustic soda, it is transformed into *isopurone*, which has acidic properties, and is readily oxidized.

The application of the electro-reduction method was at first attended by many difficulties, yields varying between wide limits being obtained, even when the process was apparently carried out in exactly the same way. Tafel has both discovered the cause of this anomaly, and indicated a method by which the reaction can be kept under control. His investigations are of interest, and are worth describing in some detail.

To be able to watch the course of the reduction-process, Tafel closed the porous cell with a stopper, through which the cathode and a delivery-tube for the gas were introduced, care being taken to make the connections air-tight. A second apparatus, exactly similar to that used for the reduction, but containing acid alone, without the purine derivative, was introduced into the same circuit. Periodically, the gas from both was collected simultaneously during one minute. The difference between these volumes of gas is a direct measure of the course of the reduction during that minute, since it indicates the quantity of hydrogen used in the reduction.

When this quantity is represented graphically, the abscissæ standing for the time which has elapsed since the beginning of the experiment, and the ordinates for the quantity of hydrogen used in the reduction, the normal course of the reduction is indicated by Fig. 70, since the quantity of hydrogen absorbed in the unit of time must diminish in the same proportion as the quantity of unreduced purine derivative.

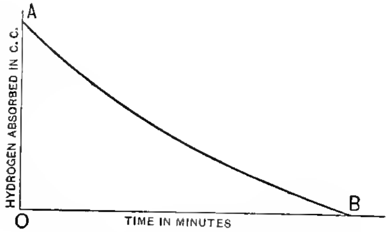


Fig. 70.—Normal Reduction-curve.

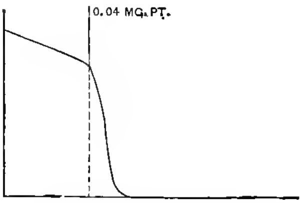


Fig. 71.—Abnormal Reduction-curve.

Tafel has, however, observed that the addition of traces of a platinum or copper salt, as well as of certain other salts, very quickly reduces the quantity of hydrogen absorbed to nearly zero.

The graphic representation in this case for the addition of 0·04 milligrammes of platinum for each 100 square centimetres of cathode surface is shown in Fig. 71. This curve indicates that the slightest contamination of the lead of the cathode by certain other metals is almost sufficient to stop the electro-reduction.

The following considerations afford an insight into the cause of this phenomenon. Hydrogen is only evolved by the passage of an electric current through dilute sulphuric acid when the contact-difference of potential between the electrodes and the solution exceeds a certain value. This is a minimum when platinum electrodes are used, and very nearly coincides with the contact-difference of potential to be expected on theoretical grounds for a reversible hydrogen—sulphuric-acid—oxygen-element.

When the cathode is made of other metals, the contact-difference of potential is greater before the evolution of hydrogen begins: for this a *supertension* (German, *Überspannung*) is necessary. This supertension has a very large value for lead, but as soon as the least trace of platinum or of certain other metals is brought into contact with the surface of the lead cathode, the supertension disappears, and with it the power possessed by the evolving hydrogen of reducing purine derivatives.

The explanation is that the contact-difference of potential regulates the energy with which the discharged ions can react, for the pressure under which a discharged ion leaves the solution depends only upon the contact-difference of potential between the electrode and the liquid in which it is immersed. Nernst states that by varying the contact-difference of potential it is possible to obtain pressures from the smallest fraction of an atmosphere up to many millions of atmospheres. Hence, reductions unattainable by other methods, and without supertension, are possible at cathodes where it exists.

SECOND PART.

THE AROMATIC COMPOUNDS, AND SUBSTANCES RELATED TO THEM.

INTRODUCTION.

281. With but few exceptions, the compounds described in the first part of this book contain an open chain. Examples of these exceptions are *cyclic* compounds such as the lactones, the anhydrides of dibasic acids, and the uric-acid group. The *closed chain* of such compounds is very readily opened, and the close relationship of their methods of formation and properties with those of the open-chain derivatives, makes it desirable to include them in a description of the aliphatic compounds.

There exists, however, a large number of substances containing closed chains of great stability towards every kind of chemical reagent, and with properties differing in many important respects from those of the aliphatic compounds. Chief among them is *benzene*, C_6H_6, with its derivatives. The molecule of benzene contains a closed chain of six carbon atoms (288): this substance and its derivatives constitute the group of *aromatic compounds*. Benzene can take up six hydrogen atoms, with formation of *hexamethylene*, C_6H_{12}, a compound also containing a closed chain of six carbon atoms, but approximating in properties to the aliphatic much more than to the aromatic group. Compounds of the formula C_nH_{2n} are also known, containing a closed chain of four or five carbon atoms: they, too, have properties similar to those of the aliphatic compounds.

The closed chain, *ring*, or *nucleus*, in benzene and its derivatives, and in the cyclic hydrocarbons C_nH_{2n}, consists of the atoms of a single element, carbon. Such compounds are called *homocyclic.*

Closed chains containing atoms of two or more elements are also known: *pyridine,* C_5H_5N, and its derivatives, have a ring containing five C-atoms and one N-atom; *furan,* C_4H_4O, four C-atoms and one O-atom; *pyrrole,* C_4H_5N, four C-atoms and one N-atom; *thiophen,* C_4H_4S, four C-atoms and one S-atom; *pyrazole,* $C_3H_4N_2$, three C-atoms and two N-atoms; and numerous other examples might be cited. Such substances are called *heterocyclic.*

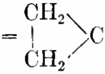
There exists another class of compounds having *condensed rings,* or two closed chains with atoms common to each. A type of these substances is *naphthalene,* $C_{10}H_8$, containing two benzene-nuclei. Two dissimilar rings can also have atoms in common, as in *quinoline,* C_9H_7N, which contains a benzene-nucleus and a pyridine-nucleus.

Since numerous derivatives of all these compounds are known, the scope of the aromatic division of organic chemistry is much more extended than that of the aliphatic division. The description of the aromatic group is, however, greatly simplified by the fact that in it the properties of alcohols, aldehydes, acids, etc., already described for the aliphatic compounds, are again met with.

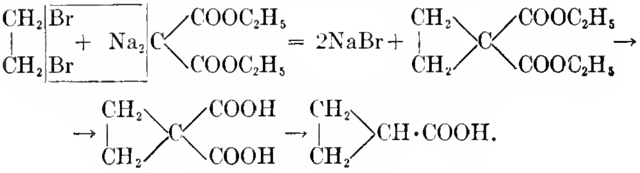
The most important cyclic compounds are benzene and its derivatives. They will be described after a brief consideration of the compounds of the formula C_nH_{2n}, containing rings of three, four, or five carbon atoms.

POLYMETHYLENE DERIVATIVES.

I. TRIMETHYLENE DERIVATIVES.

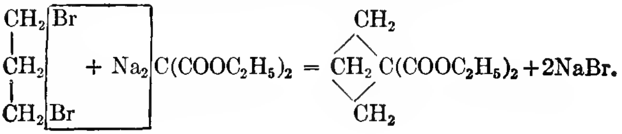
282. *Trimethylene*, C_3H_6 =  is obtained by the action of sodium on trimethylene bromide, $CH_2Br \cdot CH_2 \cdot CH_2Br$ (154). It is a gas, which liquefies at a pressure of five to six atmospheres. It is not identical with propylene, $CH_2{:}CH \cdot CH_3$, since with bromine it forms an addition-product only very slowly under the influence of sunlight, yielding trimethylene bromide. This reaction and its synthesis prove its constitution.

Trimethylenecarboxylic acid is formed by saponifying the primary product of the interaction of ethylene bromide and ethyl disodiomalonate, and eliminating carbon dioxide:



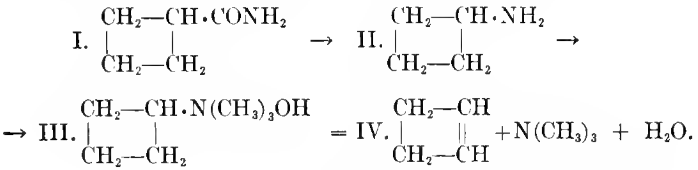
II. TETRAMETHYLENE DERIVATIVES.

283. *Tetramethylene derivatives* are obtained when diethyl disodiomalonate reacts with trimethylene bromide, the diethyl ester of a *tetramethylenedicarboxylic acid* being formed:



When heated, the dibasic acid obtained by the saponification of this ester loses one molecule of carbon dioxide (166), yielding tetramethylenecarboxylic acid.

Tetramethylene or *cyclobutane* is obtained from this acid by a method applicable to the preparation of other hydrocarbons. The amide of acid I. is converted by the method of 264 into *cyclobutylamine* (II.). Treatment of this amine with excess of methyl iodide yields the iodide of the quaternary ammonium base III., from which the base is then prepared. On dry distillation, it decomposes (73) into trimethylamine, water, and *cyclo*butylene (IV.):

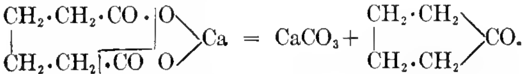


On careful reduction with hydrogen and nickel, *cyclo*butylene is converted into *cyclo*butane.

III. PENTAMETHYLENE DERIVATIVES.

284. *Pentamethylene derivatives* can be obtained by a similar method, the action of tetramethylene bromide on diethyl disodiomalonate.

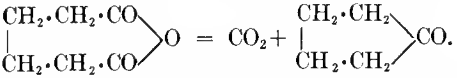
When calcium adipate is submitted to dry distillation, a keto-derivative of *pentamethylene* is formed:



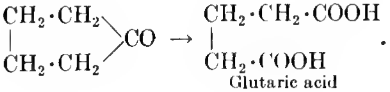
Calcium adipate

Ketopentamethylene

It is also obtained by heating adipic anhydride:

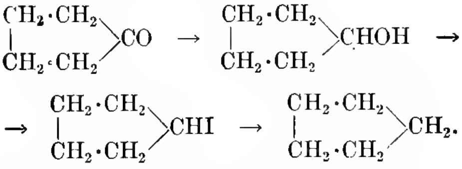


The structure of this compound is proved by its oxidation to glutaric acid:



Glutaric acid

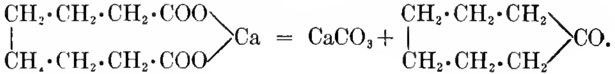
Penthamethylene is obtained by the reduction of this ketonic derivative, the carbonyl-group taking up two H-atoms, with formation of a CHOH-group. By treatment with hydriodic acid, hydroxyl is first replaced by iodine, and finally by hydrogen:



Pentamethylene is a colourless liquid boiling at 50°.

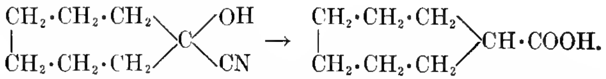
Hexamethylene and its derivatives form the group of *hydro-aromatic compounds*. On account of their relationship to the terpenes and camphors, they are described in a separate chapter (407–411).

285. Several methods are applicable to the preparation of substances containing rings of seven carbon atoms. The first member of this class to be prepared was *suberone*, obtained by the dry distillation of calcium suberate:

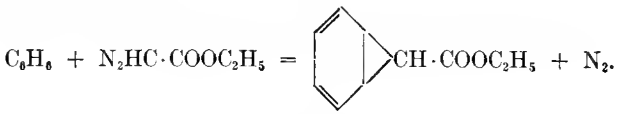


Calcium suberate Suberone

Hydrolysis of the nitrile obtained by addition of hydrocyanic acid to suberone and reduction of the resulting α-hydroxy-acid yield *suberanecarboxylic acid:*

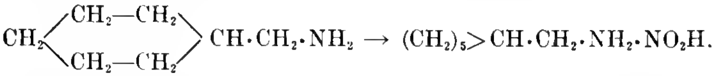


This acid is also obtained by the interaction of ethyl diazoacetate and benzene, *ethyl* pseudo*phenylacetate* being formed as an intermediate product:



The acid corresponding with this ester can be transformed into the isomeric iso*phenylacetic acid*: reduction converts this isomeride into suberanecarboxylic acid, proving the presence of an unsaturated ring of seven carbon atoms.

A third mode of preparing cyclic compounds with seven carbon atoms is exemplified by the conversion of *cyclo*hexylmethylamine (I.) and other similar primary amines into stable nitrites (II.):



$$CH_2\left\langle\begin{matrix}CH_2-CH_2\\ CH_2-CH_2\end{matrix}\right\rangle CH\cdot CH_2\cdot NH_2 \rightarrow (CH_2)_5{>}CH\cdot CH_2\cdot NH_2\cdot NO_2H.$$

On boiling in acetic-acid solution, these nitrites are transformed by elimination of nitrogen into the alcohols of the next higher ring-system:

$$(CH_2)_5{>}CH\cdot CH_2\cdot NH_2\cdot NO_2H \rightarrow (CH_2)_6{>}CHOH.$$

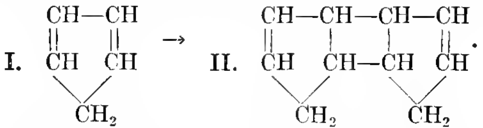
The conversion into suberone by oxidation of the alcohol formed from *cyclo*hexylmethylamine affords a proof of the course of this reaction. The synthesis of cyclic compounds containing eight carbon atoms is effected similarly.

The cyclic hydrocarbons, C_nH_{2n}, from cyclo*propane* to cyclo-*octane* have been definitely isolated. The table contains a comparison of some of their physical constants with the corresponding constants of the normal hydrocarbons of the saturated series C_nH_{2n+2}, and the unsaturated series, C_nH_{2n}.

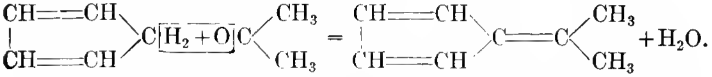
Number of Carbon Atoms.	C_nH_{2n+2}		C_nH_{2n}, Unsaturated.		C_nH_{2n}, Cyclic.	
	Boiling-point.	Specific Gravity	Boiling-point.	Specific Gravity.	Boiling-point.	Specific Gravity, d°_4
3	−45°	0·536 (0°)	− 48·2°		*ca.*–35°	
4	1°	0·600 (0°)	− 5°		11°–12°	0·7038
5	36·3°	0·627 (14°)	35°	0·648 (0°)	49°	0·7635
6	68·9°	0·658 (20°)	68°	0·683 (15°)	81°	0·7934
7	98·4°	0·683 (20°)	98°	0·703 (19·5°)	117°	0·8252
8	125·6°	0·702 (20°)	124°	0·722 (17°)	147°	0·850

The saturated cyclic hydrocarbons have higher boiling-points and much higher specific gravities (about 0·21) than their unsaturated isomerides. The saturated hydrocarbons contain two hydrogen atoms more than the corresponding olefines. The corresponding members of both series have almost the same boiling-points, but their specific gravities are about 0·02 lower.

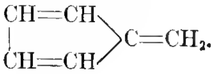
286. cyclo*Pentadiene,* C_5H_6, is a hydrocarbon which can be isolated from the first runnings obtained in the purification of crude benzene. It boils at 41°, and polymerizes readily to *dicyclopentadiene,* $C_{10}H_{12}$. *Cyclo*pentadiene forms an addition-product with four halogen atoms. Since its molecule contains six hydrogen atoms less than the corresponding saturated hydrocarbon, C_5H_{12}, the fact that it takes up four instead of six univalent atoms indicates that it has cyclic formula I.


I. *cyclo*Pentadiene II. Di*cyclo*pentadiene

Thiele found that the hydrogen of the CH_2-group in *cyclo*pentadiene can be readily substituted, and attributed its reactivity to the proximity of the two double bonds. Thus, in presence of alkalis this hydrocarbon forms remarkable condensation-products with ketones:



Thiele has named the simplest member of this group *fulvene.* Its formula is C_6H_6, so that it is isomeric with benzene. Its constitution is represented by



CONSTITUTION OF BENZENE.

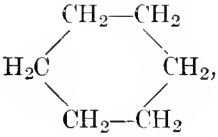
287. Certain substances found in the vegetable kingdom are characterized by the possession of an agreeable aroma: such are *oil of bitter almonds, oil of carraway, oil of cumin, balsam of Tolu, gum-benzoïn, vanilla*, etc. These vegetable-products consist principally of substances of somewhat similar character, which differ from the aliphatic compounds in containing much less hydrogen in proportion to the other elements: thus, *cymene*, $C_{10}H_{14}$, is obtained from oil of carraway; *toluene*, C_7H_8, from balsam of Tolu; and *benzoïc acid*, $C_7H_6O_2$, from gum-benzoïn. The saturated aliphatic compounds with the same number of C-atoms have the formulæ $C_{10}H_{22}$, C_7H_{16}, and $C_7H_{14}O_2$, respectively.

Before the nature of the so-called *aromatic* compounds had been closely investigated, and on account of their external similarity, it was customary to regard them as members of a single group, just as ordinary butter and "butter of antimony," $SbCl_3$, were classed together because of their similarity in consistency. This method of classification is still adopted for compounds with analogous properties, but of imperfectly understood constitution, such as the bitter principles, some vegetable alkaloids, and many vegetable dyes.

A closer study of the aromatic compounds has shown that the old and somewhat arbitrary classification according to external resemblance is well founded, since all these substances may be looked upon as derivatives of one hydrocarbon, *benzene*, C_6H_6, just as the aliphatic compounds can be regarded as derived from methane, CH_4. Thus, on oxidation, toluene yields benzoïc acid, the calcium salt of which is converted into benzene by distillation with lime. The dibasic terephthalic acid, $C_8H_6O_4$, is formed by the oxidation of cymene, and can be similarly transformed into benzene.

The discovery of this relation by Kekulé brought into prominence the question of the constitution of benzene, the basis of all the aromatic compounds. Its formula, C_6H_6, contains eight hydrogen atoms less than that of the saturated paraffin with six C-atoms, hexane, C_6H_{14}. Benzene, like other hydrocarbons poor in hydrogen, such as C_6H_{12} and C_6H_{10}, might be supposed to contain multiple carbon bonds, but its properties do not admit of this assumption. Compounds with a multiple carbon bond readily form addition-products with the halogens, are very sensitive to oxidizing agents, and easily react with von Baeyer's reagent (123): benzene lacks these properties. It yields halogen addition-products very slowly, whereas compounds with a multiple carbon bond form them instantaneously. It must, therefore, be concluded that benzene does not contain multiple carbon bonds, and that the carbon atoms in its molecule are linked together in a special manner.

Other considerations lead to the same conclusion. Von Baeyer has discovered certain dibasic acids, derivable from *hexamethylene* or cyclo*hexane*,



by exchange of hydrogen for carboxyl. Removal of two or four hydrogen atoms from these hexamethylene derivatives yields compounds the behaviour of which indicates that they contain a multiple carbon bond. The abstraction of six hydrogen atoms would be expected to produce a compound of an even more unsaturated character, but a benzene derivative lacking all the properties conferred by a double bond is formed instead. The elimination of the third pair of hydrogen atoms from the hexamethylene derivative, unlike that of the first and second pair, occasions a sudden and complete change in properties.

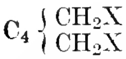
288. To understand the manner of linking of the benzene carbon atoms, it is necessary to know the relative distribution of its hydrogen and carbon atoms. Two facts suffice to determine this distribution. First, *there are no isomerides of the monosubstitution-products of benzene.* Second, *the disubstitution-products exist in three isomeric forms.* Hence, there is only one monobromobenzene, C_6H_5Br; but three dibromobenzenes are known, and are distinguished by the prefixes *ortho, meta,* and *para.*

It follows from the first of these facts that *the six hydrogen atoms of benzene are of equal value* (404): that is, replacement of any one of them yields the same monosubstitution-product. Three formulæ, in which the six hydrogen atoms are of equal value, are possible for benzene:

$$\text{I. } C_4(CH_3)_2; \quad \text{II. } C_3(CH_2)_3; \quad \text{III. } (CH)_6.$$

It has now to be considered which of these formulæ agrees with the second fact stated over-leaf.

A disubstitution-product of a compound with formula I. can be either



$$C_4\left\{\begin{matrix}CH_2X\\CH_2X\end{matrix}\right.$$

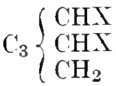
or

$$C_4\left\{\begin{matrix}CHX_2\\CH_3\end{matrix}\right..$$

No other isomerides are possible, so that this formula is inadmissible as leading to two, instead of to three, isomerides.

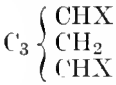
With formula II. four isomerides seem possible:

a.



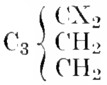
$$C_3\left\{\begin{matrix}CHX\\CHX\\CH_2\end{matrix}\right.$$

b.



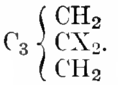
$$C_3\left\{\begin{matrix}CHX\\CH_2\\CHX\end{matrix}\right.$$

c.



$$C_3\left\{\begin{matrix}CX_2\\CH_2\\CH_2\end{matrix}\right.$$

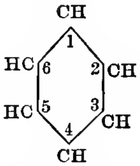
d.



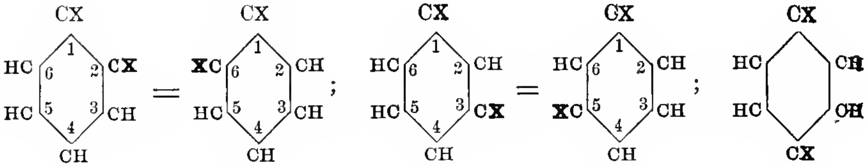
$$C_3\left\{\begin{matrix}CH_2\\CX_2.\\CH_2\end{matrix}\right.$$

The hydrogen atoms in benzene being equivalent, the CH_2-groups in the benzene molecule must be similarly linked, so that $a=b$, and $c=d$: in other words, the number of possible isomerides is reduced to two. Formula II. cannot be accepted either, since it also fails to explain the formation of three isomeric disubstitution-products.

There remains only formula III., in which each carbon atom is in union with one hydrogen atom. The question of the constitution of benzene therefore narrows itself to this: given a compound C_6H_6, in which each carbon atom is linked to one hydrogen atom, the problem is to find a formula which accounts for the equivalence of all the hydrogen atoms, the formation of three disubstitution-products, and the absence of double or multiple bonds. It is evident that an open carbon-chain formula cannot fulfil the prescribed conditions, since the hydrogen atoms attached to such a chain containing terminal and intermediate CH-groups could not be equivalent. The six hydrogen atoms can only be of equal value with a ring of six C-atoms:



This arrangement of the CH-groups also fulfils the second condition, as is evident from the scheme:



in which the compounds $C_6H_4X_2$, 1:2 = 1:6, 1:3 = 1:5, and 1:4 are isomeric. The formation of three isomerides is, therefore, also accounted for.

In this scheme, each carbon atom is in union with one hydrogen atom and two other carbon atoms, so that three bonds of each carbon atom are accounted for: it only remains to ascertain the mode of linking of the fourth carbon bond. A hypothetical view was suggested by Armstrong, and also by von Baeyer. They assume that the direction of the fourth bond of each C-atom is towards the centre of the benzene-ring, and that each bond is kept in equilibrium by the others, their mutual attraction occasioning the stability of the ring. This *centric* formula for benzene is given in Fig. 72.

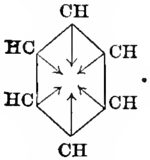


Fig 72.—Centric Formula for Benzene.

Such a mode of linking is unknown in the aliphatic series, so that it must be the cause of the properties peculiar to aromatic compounds, and lacked by those of the aliphatic group. Hence, this structural formula not only accounts for the isomerism of the derivatives of benzene, but also explains the "aromatic" character peculiar to them.

289. Although in many respects the centric formula expresses the properties of the aromatic compounds, it is not wholly satisfactory. In this regard it resembles all the other numerous benzene-formulæ which have been suggested. Fig. 73 represents the relative positions in space of the carbon atoms in the centric formula. It indicates that the carbon atoms are closely united, and thus accounts for the stability of the benzene-ring. The near proximity, however, of the *meta*-hydrogen atoms and the *para*-hydrogen atoms shows that they, like the *ortho*-hydrogen atoms, should be replaceable by one bivalent element or group. A more important objection is that according to this formula benzene derivatives with two dissimilar substituents should exist in two configurations, whereas no example of such isomerism has been observed. Moreover, the analogous spacial formulæ for naphthalene and other condensed hydrocarbons are very improbable.

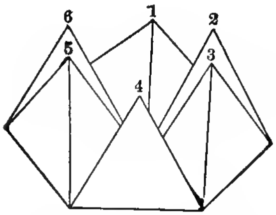


Fig. 73.—Spacial Representation of von Baeyer's Benzene-formula.

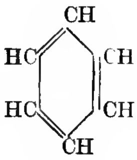


Fig. 74.—Kekulé's Benzene-formula.

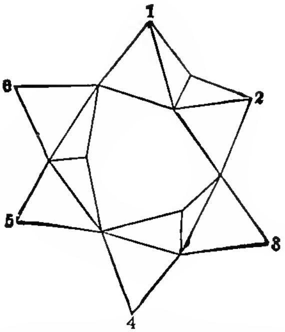


Fig. 75.—Spacial Representation of Kekulé's Benzfne-formula.

These objections do not apply to Kekulé's formula (Fig. 74), which is represented in space in Fig. 75. For many years it was accepted as a correct expression of the constitution of benzene, but there are two important reasons against it. First, it represents the *ortho*-positions, such as 1:2 and 1:6, as dissimilar, one pair of carbon atoms having between them a single, and the other pair a double, bond. Second, it contains three double bonds, whereas benzene lacks all the properties characteristic of unsaturated compounds.

To remove the first of these difficulties, KEKULÉ suggested that the double bonds of the benzene-nucleus are very readily transposed: the second has been met by a special assumption regarding the nature of the double bond. THIELE's formula for benzene is given in Fig. 76. He has made a special study of substances containing a conjugated linking (134), and has found that addition of two univalent atoms to such compounds often converts them into others with a double bond at the centre:

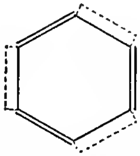
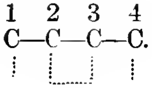


FIG. 76.—THIELE'S BENZENE-FORMULA.

$$C{=}C{-}C{=}C \rightarrow C{-}C{=}C{-}C.$$

To explain this phenomenon, he assumes that the whole of the affinity of each double bond is not satisfied, but that a part of each remains free, and unites between C-atoms 2 and 3, as indicated in the scheme



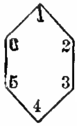
$$\overset{1}{C}{-}\overset{2}{C}{-}\overset{3}{C}{-}\overset{4}{C}.$$

The dotted lines denote *partial valencies.* There is a double bond between C-atoms 2 and 3, but it is *inactive,* since addition takes place only at 1 and 4.

In accordance with this conception, KEKULÉ's benzene-formula has three inactive double bonds, but lacks free partial valencies (Fig. 76): it therefore explains the difference between the properties of benzene and those of other unsaturated compounds.

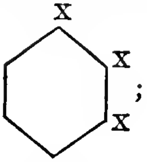
Nomenclature and Isomerism of the Benzene Derivatives.

290. The different isomeric disubstitution-products are distinguished by the prefixes *ortho, meta,* and *para*, or the positions of their substituents are denoted by numbers:

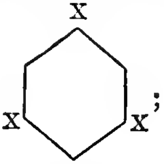


1:2 = 1:6 substitution-products are called *ortho*-compounds.
1:3 = 1:5 ,, ,, ,, ,, *meta*-compounds.
1:4 ,, ,, ,, ,, *para*-compounds.

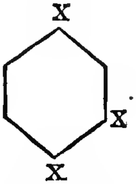
The number of isomeric substitution-products is the same for two similar or dissimilar substituents, but not for three. When the three groups are similar, three isomerides exist:



Adjacent or Vicinal
1:2:3



Symmetrical
1:3:5



Unsymmetrical
1:3:4

When one of the groups is dissimilar to the other two, different vicinal derivatives result by substitution at 2 and at 3 respectively, and, for the unsymmetrical compound, substitution at 3 produces a different compound from that resulting on exchange at 4. For four similar groups the same number (three) of isomerides is possible as for two, since the two remaining hydrogen atoms can be in the *ortho*-position, *meta*-position, or *para*-position to one another. The number of isomerides possible in other cases can be readily determined.

An alkyl-radical or other group linked to a benzene-residue, as in $C_6H_5\cdot CH_3$ or $C_6H_5\cdot CH_2\cdot CH_2\cdot CH_3$, is called a *side-chain*, the benzene-residue being called the *nucleus*. Substitution can take place both in the nucleus and in the side-chain· when in the former, it is usual to refer to the *position* of the substituent relative to those already present, the determination of which is called the *determination of position*, or *orientation*, of the substituents. The methods of orientation are given in 398 to 403.

PROPERTIES CHARACTERISTIC OF THE AROMATIC COMPOUNDS: SYNTHESES FROM ALIPHATIC COMPOUNDS.

291. The saturated hydrocarbons of the aliphatic series are not attacked by concentrated nitric acid or sulphuric acid, and only to a small extent by oxidizing agents: their halogen-substituted derivatives react with great ease. The aromatic hydrocarbons differ from the aliphatic hydrocarbons in all these respects.

1. The aromatic hydrocarbons are readily attacked by concentrated nitric acid, with formation of *nitro-compounds:*

$$C_6H_5\cdot\boxed{H+HO}NO_2 = \underset{\text{Nitrobenzene}}{C_6H_5\cdot NO_2}+H_2O.$$

These substances yield amino-derivatives on reduction, and are consequently true nitro-compounds.

2. On treatment with concentrated sulphuric acid, the aromatic compounds yield *sulphonic acids:*

$$C_6H_5\cdot\boxed{H+HO}\cdot SO_3H = \underset{\text{Benzenesulphonic acid}}{C_6H_5\cdot SO_3H}+H_2O.$$

The sulphur of the SO_3H-group is linked to a carbon atom of the benzene-nucleus, since thiophenol, $C_6H_5\cdot SH$, also yields benzenesulphonic acid on oxidation:

$$C_6H_5\cdot SH \rightarrow C_6H_5\cdot SO_3H.$$

3. The aromatic hydrocarbons with side-chains are oxidized without difficulty to acids, the whole side-chain being usually oxidized to the carbon atom in union with the nucleus, with formation of carboxyl.

4. Chlorobenzene and bromobenzene have their halogen atoms so firmly attached to the phenyl-group, C_6H_5, that they are almost incapable of taking part in double decompositions with such compounds as metallic alkoxides, salts, and so on.

292. Two syntheses of aromatic from aliphatic compounds are cited here: other examples are given in the chapter on hydrocyclic derivatives (407–411).

1. When the vapours of volatile aliphatic compounds are passed through a red-hot tube, aromatic substances are among the products. The condensation of acetylene, C_2H_2, to benzene is a typical example, although passage through a red-hot tube transforms benzene-vapour into acetylene, proving that both reactions are incomplete. A synthesis of benzene from carbon monoxide is described in 355.

2. On treatment with sulphuric acid, acetone is converted into *mesitylene*, or 1:3:5-trimethylbenzene (295):

$$3C_3H_6O - 3H_2O = C_9H_{12}.$$

Other ketones condense similarly to aromatic hydrocarbons.

BENZENE AND THE AROMATIC HYDROCARBONS WITH SATURATED SIDE-CHAINS.

Gas-manufacture and its By-products: Tar.

293. The aromatic hydrocarbons are employed in large quantities in the manufacture of coal-tar colours, and are obtained from coal-tar, a by-product in the manufacture of gas. A short description of this process will not be out of place, since it also yields other products of importance in the organic chemical industry.

Coal is gradually heated in iron retorts of ⌓-shaped cross-section, and is finally raised to a red heat: the gases and vapours are removed as completely as possible by means of exhaust-pumps. *Coke* remains in the retorts, and is employed as fuel and in many metallurgical processes, although for the latter purpose the coke has usually to be prepared by special means.

The distillate contains three main products. 1. Gases (illuminating-gas). 2. An aqueous liquid, containing ammonia and other basic substances, such as pyridine bases. 3. Tar. These products are separated from one another as completely as possible by a series of treatments. The crude gas is passed over iron-ore and lime, to remove the cyanogen derivatives and sulphur compounds. The former purifying material is employed subsequently for the preparation of potassium ferrocyanide (**263**), an important source of the cyanogen compounds.

Tar is a thick, black liquid with a characteristic odour. Its colour is due to suspended particles of carbon. It is a complicated mixture of neutral, acidic, and basic substances. The first are principally hydrocarbons, chiefly belonging to the aromatic series. About 5–10 per cent. of the tar consists of naphthalene, and 1–1·5 per cent. of a mixture of benzene and toluene. Phenol (**304**) is the principal acidic constituent of tar. Basic substances are present only in small proportion: the chief are pyridine, quinoline, and their homologues.

In the arts, the separation of the tar-products is effected partly by chemical means, and partly by fractionation. The tar is first distilled, a considerable portion remaining in the retort as a black, somewhat brittle mass, known as *pitch.* From the distillate, the phenol, or carbolic acid, is removed by careful treatment with caustic alkali, and the basic substances by means of acid. The residue is distilled, four fractions being obtained.

1. Light oil, distilling up to 170°
2. Carbolic oil, between 170° and 230°.
3. Heavy oil, or creosote-oil, between 230° and 270°.
4. Anthracene-oil, above 270°.

The light oil contains benzene and its homologues, which can be separated by further fractionation. Only a limited number of the homologues of benzene are present in the light oil—principally *toluene,* or methylbenzene, and *xylene,* or dimethylbenzene.

Methods of Formation.

294. 1. Fittig's synthesis is carried out by treating bromobenzene, or, in general, a hydrocarbon containing bromine in the nucleus, with an alkyl bromide or iodide and sodium (**31**):

$$\begin{array}{r} C_6H_5 \\ + \end{array}\boxed{\begin{array}{ll} Br + & Br \\ Na & Na \end{array}}C_2H_5 = \underset{\text{Ethylbenzene}}{C_6H_5\text{—}C_2H_5} + 2NaBr.$$

A series of by-products is sometimes obtained, among them paraffins and diphenyl, $C_6H_5 \cdot C_6H_5$. The yield of alkylbenzene is, however, very good when the higher normal primary alkyl iodides are employed.

2. Friedel and Crafts's synthesis is peculiar to the aromatic series, and depends upon a remarkable property of aluminium chloride. This substance is obtained by the action of dry hydrochloric-acid gas on aluminium-foil. On bringing it into contact with a mixture of an aromatic hydrocarbon and an alkyl chloride, clouds of hydrochloric acid are evolved, and hydrogen of the nucleus is exchanged for the alkyl-group:

$$C_6H_5 \cdot \boxed{H + Cl}CH_3 = C_6H_5 \cdot CH_3 + HCl.$$

In the synthesis of **Friedel** and **Crafts** more than one alkyl-group is generally introduced, the monosubstitution-products and the higher substitution-products being simultaneously formed: the mixture is separated by fractional distillation.

This reaction constitutes a method both for the building-up and breaking-down of a hydrocarbon. When toluene, $C_6H_5\cdot CH_3$, is treated with aluminium chloride, benzene, C_6H_6, and xylene, $C_6H_4(CH_3)_2$, are formed. The alkyl-groups of one hydrocarbon are exchanged for the hydrogen of the other. The reaction can also be effected by the action of concentrated sulphuric acid upon aromatic hydrocarbons with a number of side-chains.

3. Like the saturated aliphatic hydrocarbons, the aromatic hydrocarbons are got by the distillation of the calcium salts of the aromatic acids with soda-lime:

$$C_6H_5\cdot\boxed{CO_2ca^* + caO}H = C_6H_6 + CaCO_3.$$

4. Benzene and its homologues can be obtained by heating the sulphonic acids with sulphuric acid or hydrochloric acid, the decomposition being facilitated by the introduction of superheated steam:

$$C_6H_3(CH_3)_2\boxed{SO_3H + HO}H = C_6H_4(CH_3)_2 + H_2SO_4.$$

This method can be employed in the separation of the aromatic hydrocarbons from the paraffins. When warmed with concentrated sulphuric acid, the former are converted into sulphonic acids, soluble in water: the paraffins are unacted upon and are insoluble in water. A mechanical separation is thus possible.

This method can also be applied to the separation of the aromatic hydrocarbons from one another, since some of them are more readily converted into sulphonic acids than others.

5. By heating an alcohol, an aromatic hydrocarbon, and zinc chloride at 270°–300°. The zinc chloride acts as a dehydrating agent:

$$C_6H_5\boxed{H + HO}\cdot C_5H_{11} = C_6H_5{-}C_5H_{11} + H_2O.$$

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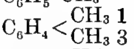
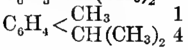
* ca $= \frac{1}{2}$Ca.

Physical Properties.

295. Benzene and the aromatic hydrocarbons with saturated side-chains are colourless, highly refractive substances, liquid at ordinary temperatures, and possessing a characteristic odour. They are immiscible with water, but mix in all proportions with strong alcohol. Some of their physical properties are indicated in the table.

Name.	Formula.	Boiling-point.	Specific Gravity.
Benzene.	C_6H_6	80·4°	0·874 (20°)
Toluene.	$C_6H_5\cdot CH_3$	110°	0·869 (16°)
m-Xylene	 $C_6H_4<\begin{smallmatrix}CH_3 & 1\\ CH_3 & 3\end{smallmatrix}$	139°	0·881 (0°)
Mesitylene.	$C_6H_3(CH_3)_3$ (1:3:5)	164°	0·865 (14°)
Ethylbenzene.	$C_6H_5\cdot C_2H_5$	136°	0·883 (0°)
*iso*Propylbenzene (Cumene)	$C_6H_5\cdot CH(CH_3)_2$	153°	0·866 (16°)
p-Methyl*iso*propylbenzene (Cymene) . . .	 $C_6H_4<\begin{smallmatrix}CH_3 & 1\\ CH(CH_3)_2 & 4\end{smallmatrix}$	175°	0·856 (20°)

Individual Members.

296. Benzene was discovered by FARADAY, in 1825, in a liquid obtained from compressed coal-gas. It melts at 5·4°.

The molecular weights of alcohols, phenols, and aliphatic acids determined by the cryoscopic method, with benzene as solvent, are sometimes twice as great as the accepted values, whereas normal results are obtained for other substances not containing a hydroxyl-group.

The formation of double and multiple molecules in solution depends in large measure upon the nature of the solvent. In addition to benzene, other hydrocarbons, acetic acid, and formic acid induce the formation of complex molecules. The results obtained with such solvents by the cryoscopic method for the determination of molecular weights are unreliable (89).

Xylene, or dimethylbenzene, exists in three isomeric forms: m-*xylene* is the principal constituent of the xylene in tar, forming 70–85 per cent. of the whole.

The isomeric xylenes are separable with difficulty: their boiling-points lie very close together, that of *o*-xylene being 142°, while *m*-xylene and *p*-xylene boil at 139° and 138° respectively. This makes their separation by fractional distillation impracticable, but it can be effected by treating them with sulphuric acid at ordinary temperatures: *m*-xylene and *o*-xylene go into solution as sulphonic acids, while *p*-xylene remains undissolved. The sulphonic acid of the *meta*-compound and that of the *ortho*-compound can be separated by fractional crystallization of their sodium salts, the *ortho*-salt crystallizing first.

Cymene, $C_{10}H_{14}$, is closely related to the terpenes $C_{10}H_{16}$, and to the camphors $C_{10}H_{16}O$, since it can be obtained from them. Cymene is a constituent of certain essential oils, such as *oil of carraway*, *oil of thyme*, and *oil of eucalyptus*.

MONOSUBSTITUTION-PRODUCTS OF THE AROMATIC HYDROCARBONS.

I. MONOSULPHONIC ACIDS.

297. The formation of these compounds is described in **291**: they are produced by the action of concentrated sulphuric acid upon aromatic compounds. In separating them from the excess of sulphuric acid, advantage is taken of the ready solubility of their calcium and barium salts in water: the process is similar to the separation of ethyl hydrogen sulphate from sulphuric acid (**60**). They can also be separated from their concentrated solutions containing sulphuric acid by the addition of common salt until no more will dissolve, when the sodium salt of the sulphonic acid precipitates in the solid state. This salt is dissolved in water, the equivalent quantity of mineral acid added, and the free sulphonic acid isolated by repeated extraction with ether.

The sulphonic acids are colourless, crystalline substances, generally hygroscopic, and freely soluble in water. They can be reconverted into the aromatic hydrocarbons by treatment at a high temperature with hydrochloric acid, or with superheated steam (**294**, 4).

Most of the sulphonates crystallize well, and are employed in the purification of the sulphonic acids. On treatment with phosphorus pentachloride, the latter are converted into chlorides:

$$C_6H_5\cdot SO_2\cdot OH \rightarrow C_6H_5\cdot SO_2\cdot Cl.$$

The *sulphonyl chlorides* are very stable towards cold water, being but slowly reconverted into sulphonic acids.

The *sulphonamides* are formed by the action of ammonium carbonate on the chlorides:

$$C_6H_5\cdot SO_2Cl \rightarrow C_6H_5\cdot SO_2\cdot NH_2.$$

They are well-crystallized compounds: the determination of their melting-points is often employed for the identification of an aromatic hydrocarbon. On account of the strongly negative character of the group $C_6H_5SO_2$—, the hydrogen atoms of the NH_2-group are replaceable by metals; hence the sulphonamides are soluble in alkalis.

On prolonged reduction, the sulphonic acids yield *thiophenols*, such as $C_6H_5 \cdot SH$, which can be reconverted by oxidation into the sulphonic acids (291, 2).

II. MONOHALOGEN COMPOUNDS.

298. Benzene does not yield isomeric monohalogen derivatives, a proof that its hydrogen atoms are of equal value (288). Toluene, $C_6H_5 \cdot CH_3$, yields *o*-, *m*-, and *p*-halogen derivatives, as well as compounds containing halogen in the side-chain. The hydrogen atoms of the side-chain are not equal in value to those attached to the nucleus, so that compounds with halogen in the side-chain should be different from those having halogen in the nucleus: experiment bears this out. The chlorine atom in monochlorobenzene can only be made to react with great difficulty. Monochlorobenzene can be boiled with alkali, with potassium hydrogen sulphide, with potassium cyanide, or can be heated with ammonia, without substitution of the halogen atom, which is only effected by a powerful reagent—sodium methoxide—at 220°. These facts prove that the halogen atom has different characteristics when in union with the nucleus and when a constituent of aliphatic halogen derivatives. FITTIG's synthesis (294, 1) is one of the few examples of its entering into reaction.

Magnesium reacts similarly with ethereal solutions of bromobenzene and alkyl halides (82). With the former a compound $C_6H_5 \cdot Mg \cdot Br$ is obtained in solution: it can be employed in the synthesis of tertiary alcohols containing the group C_6H_5, as described in 111.

The behaviour of *benzyl chloride*, C_7H_7Cl, obtained by the action of chlorine upon boiling toluene, is in marked contrast to that of monochlorobenzene. It reacts as readily with the alkalis, ammonia, potassium cyanide, and silver salts, as do the aliphatic halogen derivatives: its halogen atom is not attached to the nucleus, but is in the side-chain. Its formula is $C_6H_5 \cdot CH_2Cl$, since, on oxidation, it yields *benzoïc acid*, $C_6H_5 \cdot COOH$, containing no chlorine. The formula $C_6H_5 \cdot CH_2Cl$ explains the similarity in character of its halogen atom to that in an aliphatic halide, for it indicates that benzyl chloride may be looked upon as methyl chloride with one hydrogen atom replaced by a phenyl-group.

There is also a difference in the external properties of these two classes of halogen derivatives: the compounds with halogen attached to the nucleus have a faint, agreeable odour, while those with halogen in the side-chain have usually a very pungent odour.

The marked difference between isomerides obtained by substitution respectively in the nucleus and in the side-chain, just described for the halogen substitution-products, is also characteristic of other derivatives of the aromatic hydrocarbons. The first have a *special* character, and the second a general resemblance to the aliphatic compounds.

Methods of Formation.

299. Chlorine and bromine can be introduced directly into the aromatic hydrocarbons. Substitution by iodine is only effected in presence of an oxidizing agent, such as iodic acid, to remove the hydriodic acid formed: its introduction is more usually accomplished by an indirect method. The experimental conditions determine whether the substituent enters the nucleus or the side-chain.

1. *Temperature.*—At low temperatures, halogens substitute in the nucleus, and at high temperatures, in the side-chain: thus, on treatment with chlorine, cold toluene yields o-*chlorotoluene* and p-*chlorotoluene;* when, however, chlorine or bromine is brought into contact with boiling toluene (110°), *benzyl chloride*, $C_6H_5 \cdot CH_2Cl$, or *benzyl bromide*, $C_6H_5 \cdot CH_2Br$, is almost exclusively formed.

2. *Halogen-carriers.*—The presence of halogen-carriers, such as aluminium chloride or ferric chloride, results in the introduction of chlorine into the nucleus, even at elevated temperatures.

3. *Sunlight.*—At ordinary temperatures, and even at 0°, chlorine or bromine substitutes exclusively in the side-chain, if the reaction-mixture be exposed to direct sunlight: thus, in the absence of light, ethylbenzene is not attacked by bromine at low temperatures, but in direct sunlight is rapidly converted into $C_6H_5 \cdot CHBr \cdot CH_3$.

Individual Members.

300. *Monochlorobenzene* is a colourless liquid: it boils without decomposition at 132°, and has a specific gravity of 1·106 at 20°. *Monobromobenzene*, B.P. 157°, sp. gr. 1·491 at 20°. *Monoiodobenzene*, B.P. 188°, sp. gr. 1·861 at 0°.

Benzyl chloride is a colourless liquid of stupefying odour, intensified by warming: it boils at 178°, and has a specific gravity of 1·113 at 15°. *Benzyl iodide* is prepared by heating benzyl chloride with potassium iodide: it melts at 24°, and decomposes when boiled. It has a powerful and unbearably irritating odour, productive of tears.

Iodobenzene, and other iodine compounds substituted in the nucleus, can add on two atoms of chlorine, with formation of substances such as *phenyliodide chloride* or *iodobenzene dichloride*, $C_6H_5\cdot ICl_2$. When digested with alkalis, these derivatives give *iodoso-compounds*, such as *iodosobenzene*, $C_6H_5\cdot IO$, which are amorphous, yellowish solids. When heated, or oxidized with bleaching-powder, these compounds yield *iodoxy-compounds* (German, *Iodoverbindungen*),

$$2C_6H_5\cdot IO = C_6H_5\cdot I + \underset{\text{Iodoxybenzene}}{C_6H_5\cdot IO_2}.$$

Iodoxybenzene is crystalline, and explodes when heated.

The constitution of these compounds is inferred from their ready conversion into iodobenzene, effected for iodosobenzene by means of potassium iodide, and for iodoxybenzene by hydrogen dioxide, with evolution of oxygen. These substances would not be so readily converted into iodobenzene if the oxygen were attached to the benzene-nucleus.

III. MONOHYDRIC PHENOLS AND AROMATIC ALCOHOLS.

301. The hydroxyl-compounds of the aromatic hydrocarbons display the same characteristic difference, caused by the attachment of the substituent to the nucleus or to the side-chain, as the halogen derivatives (298). The OH-group in *phenol*, $C_6H_5\cdot OH$, is linked to the nucleus, and possesses a character unknown in the fatty series. A compound such as *benzyl alcohol*, $C_6H_5\cdot CH_2OH$, the constitution of which follows from its oxidation to benzoïc acid, $C_6H_5\cdot COOH$, displays most of the properties characteristic of the aliphatic alcohols.

A. PHENOLS.

302. Phenol and some of its homologues, such as *cresol* and others, are found in coal-tar. During its fractional distillation they are accumulated in the carbolic oil and creosote-oil (**293**). They are isolated by agitating these fractions with caustic alkali, which dissolves the phenols, leaving the hydrocarbons. They are liberated from the solution with sulphuric acid, and are then separated by fractional distillation. By far the larger proportion of the phenol of commerce is obtained from this source.

Phenol and its homologues can also be obtained by other methods.

1. By fusion of the salt of a sulphonic acid with alkali:

$$C_6H_5 \cdot SO_3K + 2KOH = C_6H_5 \cdot OK + K_2SO_3 + H_2O.$$

2. By the action of nitrous acid on aromatic amines, a method analogous to the preparation of alcohols of the aliphatic series from amines (**72**). But whereas on treating an aliphatic amine with nitrous acid the alcohol is produced directly, in this reaction very important intermediate products, the diazonium compounds (**339**), can be isolated.

3. By the action of oxygen upon benzene in presence of aluminium chloride, phenol is formed.

Properties of the Phenols.

303. The phenols are in some respects comparable with the tertiary alcohols, since in both the hydroxyl is linked to a carbon atom in direct union with three others, although in the phenols one of these bonds is of a special kind. Like the tertiary alcohols, therefore, they cannot be oxidized to aldehydes, ketones, or acids containing the same number of C-atoms. The phenols exhibit many of the characteristics of the aliphatic alcohols: they form ethers by the interaction of alkyl halides and their alkali-metal salts; they produce esters, forming, for example, acetates with acetyl chloride. Phosphorus pentachloride causes the exchange of Cl for their OH, although not so readily as in the aliphatic series. But in addition to these properties, the phenols possess special characteristics due to their much stronger acidic character. When describing the separation of phenols from carbolic oil (**293**), it was mentioned that they dissolve in caustic alkalis: *phenoxides,* such as $C_6H_5 \cdot ONa$, are formed. The alcohols of the aliphatic series do not possess this property in the same degree. If they are insoluble in water, they do not dissolve in caustic alkalis, and are only converted into metallic alkoxides by the action of the alkali-metals. This increase in acidic character can only be occasioned by the presence of the phenyl-group; in other words, *the phenyl-group has a more negative character than an alkyl-group.* Otherwise, the phenols behave as weak acids: their aqueous solutions are bad conductors of electricity, and the phenoxides are decomposed by carbonic acid.

It is thus evident that the properties of the hydroxyl-group are considerably modified by union with the phenyl-group. Inversely, the influence of the hydroxyl-group on the benzene-nucleus is equally marked: it makes the remaining hydrogen atoms much more readily substituted. Benzene is only slowly attacked by bromine at ordinary temperatures, but the addition of bromine-water to an aqueous solution of phenol at once precipitates 2:4:6-*tribromophenol*—a reaction employed in its quantitative estimation. The conversion of benzene into nitrobenzene necessitates the use of concentrated nitric acid, but phenol yields nitrophenol on treatment with the dilute acid. Phenols are also much more readily oxidized than the aromatic hydrocarbons.

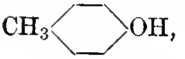
On distillation with zinc-dust, the phenols are reduced to the corresponding hydrocarbons. They can be detected by the formation of a violet coloration when ferric chloride is added to their aqueous solutions.

Individual Members.

304. *Phenol,* or *carbolic acid,* is a colourless substance, crystallizing in long needles. It melts at 39·6°, and boils without decomposition at 181°. It has a characteristic odour, and strong antiseptic properties. It was formerly largely employed in surgery, but to a great extent its place has been taken by mercuric chloride. Phenol is soluble in water, 1 part dissolving in 15 at 16°: it can also dissolve water. On account of the small molecular weight of water, and the high molecular depression of phenol (75), a small percentage of water renders phenol liquid at ordinary temperatures (14). It follows from the equation $AM = 75$, in which M is the molecular

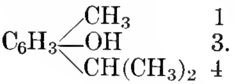
weight of water (18), that Δ, the lowering of the freezing-point occasioned by the presence of 1 per cent. of water, is about 4·2°.

The hydroxytoluenes, $CH_3 \cdot C_6H_4 \cdot OH$, are called *cresols:* they are present in coal-tar, but are usually prepared from the corresponding amino-compounds or sulphonic acids. On oxidation, they are completely decomposed, but when the hydrogen of the hydroxyl-group is replaced by alkyl or acetyl, they can, like toluene itself, be oxidized to the corresponding acids. The cresols resemble phenol in their behaviour towards bromine-water. p-*Cresol,*



is a decomposition-product of albumin.

Thymol is also used as an antiseptic. It is hydroxycymene,



$$C_6H_3\begin{cases} CH_3 & 1 \\ OH & 3. \\ CH(CH_3)_2 & 4 \end{cases}$$

Acid sulphuric esters of phenol are present in urine: they result from the fermentation (putrefaction) of proteïns, since the proportion present depends upon the extent of this process.

B. AROMATIC ALCOHOLS.

305. *Benzyl alcohol*, $C_6H_5 \cdot CH_2OH$, is the typical aromatic alcohol: it possesses nearly all the properties of an aliphatic alcohol. It can be obtained by treatment of benzyl chloride with potassium acetate, and saponification of the ester of acetic acid thus formed. It can also be prepared by electro-reduction of benzoïc acid in sulphuric-acid solution with lead cathodes. It reacts readily with phosphorus pentachloride, yielding benzyl chloride, and forms esters, ethers, etc.: being a primary alcohol, it can be oxidized to the corresponding aldehyde, *benzaldehyde* (335), and also to *benzoïc acid* (331). It differs from the aliphatic alcohols in its behaviour towards sulphuric acid, which causes resinification, instead of the formation of the corresponding sulphuric ester. Benzyl alcohol possesses no phenolic properties: it is insoluble in alkalis, and does not yield the characteristic phenol coloration with ferric chloride.

Benzyl alcohol is a liquid which dissolves with difficulty in water: it boils at 206°, and possesses only a faint odour.

IV. SULPHUR DERIVATIVES.

306. *Thiophenol*, $C_6H_5 \cdot SH$, boils at 172·5°. It can be obtained by heating phenol with phosphorus pentasulphide, P_2S_5, or by reduction of the chloride of benzenesulphonic acid. It has all the properties of the mercaptans, particularly the power of forming salts. Like the most volatile sulphur compounds, it has a disagreeable odour.

Sulphur compounds similar to those described in the aliphatic series (**67** and **68**) are also known in the aromatic series; such are thioethers, sulphones, and sulphinic acids.

V. ETHERS.

307. A distinction is drawn between the aromatic-aliphatic ethers, such as *anisole*, $C_6H_5 \cdot O \cdot CH_3$, and the true aromatic ethers, like phenyl ether, $C_6H_5 \cdot O \cdot C_6H_5$. Compounds of the first class are formed by the interaction of alkyl halides and phenoxides (**303**):

$$C_6H_5 \cdot O \cdot \boxed{Na + I} C_2H_5 = C_6H_5 \cdot O \cdot C_2H_5 + NaI.$$

The true aromatic ethers cannot be prepared by this method, since the halogen atom attached to the nucleus is exchanged only with difficulty (**298**). Phenyl ether is obtained by heating phenol with a dehydrating agent, such as chloride of zinc or of aluminium:

$$C_6H_5 \cdot \boxed{OH + H} O \cdot C_6H_5 = C_6H_5 \cdot O \cdot C_6H_5 + H_2O.$$

The mixed aromatic-aliphatic ethers are stable compounds, and resemble the true aliphatic ethers closely in behaviour. Many of their reactions are similar to those of the aromatic hydrocarbons themselves. When heated to a high temperature with a hydrogen halide, they yield a phenol and an alkyl halide (**64**):

$$\underset{\text{Anisole}}{C_6H_5 \cdot O \cdot CH_3} + HI = C_6H_5 \cdot OH + CH_3 \cdot I.$$

The true aromatic ethers, such as phenyl ether, are not decomposed by hydriodic acid, even at 250°.

Anisole, $C_6H_5 \cdot O \cdot CH_3$, is a liquid, and boils at 155°. *Phenetole*, $C_6H_5 \cdot O \cdot C_2H_5$, is also a liquid, and boils at 172°. Each has a characteristic odour.

VI. MONONITRO-DERIVATIVES.

308. A point of characteristic difference between the aromatic and aliphatic compounds is that the former are very readily converted into nitro-derivatives by the action of concentrated nitric acid (**291**, 1). This is the only method employed in practice for the preparation of aromatic nitro-compounds. The substance is treated with a mixture of nitric acid and sulphuric acid:

$$C_6H_5\cdot\boxed{H+HO}\cdot NO_2 = C_6H_5\cdot NO_2+H_2O.$$

If the sulphuric acid were not present, the water formed in the nitration would dilute the nitric acid and retard the action. Increase in the number of alkyl-groups attached to the benzene-nucleus is often accompanied by a corresponding increase in the ease with which nitration is effected.

Properties.

309. The mononitro-compounds are very stable, and can be distilled without decomposition: their nitro-groups are very firmly attached to the nucleus. Unlike the primary and secondary nitro-compounds of the aliphatic series, the aromatic nitro-derivatives do not contain hydrogen replaceable by metals, since their nitro-group is linked to a tertiary carbon atom: such an exchange is therefore impossible (**76**). On reduction, the nitro-compounds yield amines, and the reaction can be modified so as to isolate various intermediate products (**321–327**).

Most of the nitro-compounds have a pale-yellow colour and an agreeable odour: they are usually liquids heavier than water, in which they are insoluble. They are volatile with steam.

Individual Members.

310. *Nitrobenzene* is manufactured in large quantities in the aniline-dye industry. Cast-iron vessels fitted with a stirring apparatus, and kept cool by water, are employed. They are charged with benzene, and into this a mixture of nitric acid and sulphuric acid is allowed to flow. At the end of the reaction, the nitrobenzene floating on the surface of the sulphuric acid, which contains only small quantities of nitric acid, is washed with water, and purified by distillation with steam.

Nitrobenzene is a yellowish liquid: it has an odour resembling that of bitter almonds, and for this reason is employed in perfumery. Its boiling-point is 208°, its melting-point 5·5°, and its specific gravity 1·1987 at 25°. Its preparation on the large scale is carried out in order to obtain *aniline* by its reduction (**313** and **326**).

Nitrotoluenes.—When toluene is nitrated, the chief products are the *ortho*-compound and *para*-compound: the *meta*-compound is only formed in traces. The relative proportion of the two isomerides produced depends upon the method of nitration. *Para-nitrotoluene*, $C_6H_4<\begin{matrix}CH_3 & 1\\ NO_2 & 4\end{matrix}$, is solid, melting at 51°, and can be obtained pure by cooling the liquid mixture of the isomerides. The *para*-compound can be removed from the liquid residue by fractional distillation, only a small percentage of it remaining in the principal fraction: pure *o-nitrotoluene* can then be isolated from it by artificial cooling.

Phenylnitromethane and the Pseudo-acids.

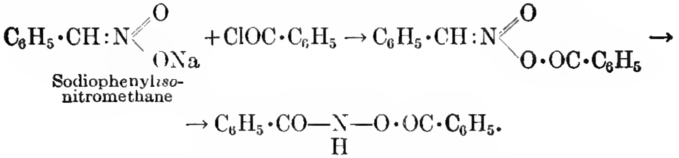
311. *Phenylnitromethane*, $C_6H_5\cdot CH_2NO_2$, is an aromatic compound with a nitro-group in the side-chain, as is evident from its formation by the action of benzyl chloride or iodide on silver nitrite:

$$C_6H_5\cdot CH_2\boxed{Cl+Ag}NO_2 = C_6H_5\cdot CH_2NO_2+AgCl.$$

It can be reduced to benzylamine, which proves it to be a true nitro-compound. Phenylnitromethane, and its derivatives with substituents attached to the nucleus, exist in two modifications which are readily transformed into each other. Phenylnitromethane is a liquid: its aqueous solution does not react with ferric chloride. After it has been converted into its sodium derivative by the action of sodium alkoxide, addition of excess of a strong mineral acid causes the separation of a crystalline substance of the same composition as phenylnitromethane: the aqueous solution of this compound gives a coloration with ferric chloride. On standing for some hours, these crystals are completely reconverted into the ordinary liquid phenylnitromethane. It is very probable that the sodium compound and the unstable modification corresponding to it have the constitutions

$$C_6H_5\cdot CH{:}NO\cdot ONa, \quad \text{and} \quad C_6H_5\cdot CH{:}NO\cdot OH.$$

The presence of a hydroxyl-group is proved by the formation of *dibenzhydroxamic acid* on treatment with benzoyl chloride:



$$C_6H_5\cdot CH:N\begin{matrix}\nearrow O\\ \searrow ONa\end{matrix} + ClOC\cdot C_6H_5 \rightarrow C_6H_5\cdot CH:N\begin{matrix}\nearrow O\\ \searrow O\cdot OC\cdot C_6H_5\end{matrix} \rightarrow$$

Sodiophenyl*iso*-nitromethane

$$\rightarrow C_6H_5\cdot CO-\underset{H}{N}-O\cdot OC\cdot C_6H_5.$$

Dibenzhydroxamic acid

Another proof of the presence of a hydroxyl-group is that *iso*nitro-compounds, unlike ordinary nitro-compounds, react vigorously with phenyl *iso*cyanate (319) at low temperatures.

From these facts it may be inferred that when phenylnitromethane, $C_6H_5\cdot CH_2NO_2$, is converted into a salt, it first changes to an isomeric modification. Inversely, when it is liberated from its sodium compound, the *iso*-modification is first produced, and slowly changes to the ordinary form.

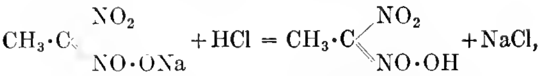
The dilute aqueous solution of m-*nitrophenylnitromethane* affords a striking example of this phenomenon. This compound is colourless, but its sodium salt has a deep-yellow colour. On the addition of an equivalent quantity of hydrochloric acid to its deeply-tinted solution, the yellow colour disappears somewhat slowly, indicating the conversion of the *iso*-compound into its normal isomeride.

The discharge of the colour is attended by another phenomenon: the electric conductivity of the liquid is considerably greater immediately after the addition of the hydrochloric acid than it is several minutes later, when the colour has nearly vanished. The explanation of this is that the *iso*-form is a true acid, and is therefore a conductor in aqueous solution, while the solution of the normal modification is a non-conductor, and therefore possesses no acidic character.

Compounds which change to an *aci*-modification on formation of metallic derivatives are called pseudo-*acids*. In addition to phenylnitromethane and its ring-substituted derivatives, other *pseudo*-acids are known, most of which were prepared by HANTZSCH.

Besides the properties indicated above, the *pseudo*-acids possess others by which they may be detected. It has just been stated that the addition of a strong acid to a *pseudo*-acid salt liberates the *pseudo*-acid, which is slowly converted into the normal modification. Inversely, the addition of an equivalent quantity of caustic alkali to the normal modification results in its gradual neutralization. This "slow neutralization" is a characteristic of the *pseudo*-acids.

Another of the characteristics by which they may be recognized is illustrated by *dinitroethane*, which, after being liberated from its sodium salt in accordance with the equation



$$CH_3\cdot C\begin{matrix}NO_2\\NO\cdot ONa\end{matrix}+HCl=CH_3\cdot C\begin{matrix}NO_2\\NO\cdot OH\end{matrix}+NaCl,$$

aci-Dinitroethane

is so rapidly converted into the normal compound, $CH_3\cdot CH<^{NO_2}_{NO_2}$, that a change in the electric conductivity of the solution can scarcely be observed even at 0°. The neutral reaction of the alkali-metal derivatives of the non-conducting or weakly-conducting hydrogen compound nevertheless indicates the existence of a *pseudo*-acid. An acid which is so weak that its solution is a bad conductor of electricity yields alkali-metal salts which undergo strong hydrolytic dissociation, and therefore have a strongly alkaline reaction ("Inorganic Chemistry," 66). Such a substance as sodiodinitroethane forms a non-alkaline solution, and must therefore be derived from an acid other than dinitroethane, since this substance has a neutral reaction and is a non-conductor in aqueous solution.

Among the other methods of detecting *pseudo*-acids is the non-formation of an addition-product with ammonia. A true acid, when dissolved in benzene or another hydrocarbon, combines instantaneously with dry ammonia to form an insoluble ammonium salt. A *pseudo*-acid, on the contrary, either does not add on NH_3, or only slowly, being in the latter case first converted into a true acid.

Another test for *pseudo*-acids is afforded by the fact that the electric conductivity of pyridine-solutions of many of them is much greater than that of aqueous solutions containing like proportions of the true acids.

VII. MONOAMINO-COMPOUNDS.

312. The amino-compounds of the aromatic series, with the NH_2-group attached to the ring, are almost exclusively obtained by reduction of the corresponding nitro-compounds. This is effected by the action of tin and hydrochloric acid, iron-filings and acetic acid or hydrochloric acid, or by other reagents. On the manufacturing scale it is usual to employ iron-filings and hydrochloric acid.

Amines can be obtained from phenols by heating them at 300° with ammonium zinc chloride.

The aromatic amines are colourless liquids of high boiling-point, or solids, and have a characteristic odour. With water, the aliphatic amines form stronger bases than ammonia, but the aqueous solutions of the aromatic amines possess only weakly basic properties: thus, they do not turn red litmus blue, and scarcely conduct an electric current. The aromatic amines yield salts, however, although these have an acid reaction in solution, on account of partial hydrolysis. The negative character of the phenyl-group, already alluded to in connection with phenol (**303**), considerably modifies the nature of the amino-group: the difference in the behaviour of diphenylamine and of triphenylamine in particular betrays this influence. With strong acids the former can yield salts, which, however, are completely hydrolyzed by the addition of a considerable quantity of water; the second does not unite with acids.

Substitution of the amino-group for hydrogen produces the same effect upon the benzene-nucleus as substitution of the hydroxyl-group for hydrogen, making the rest of the hydrogen atoms of the nucleus much more easily replaced: thus, aniline is readily converted by bromine-water into 2:4:6-tribromoaniline. Moreover, the amines are much more readily oxidized than the hydrocarbons.

By means of an alkyl halide, the hydrogen atoms in the amino-group of the primary aromatic amines, like those in the amino-group of the primary aliphatic amines, can be replaced by an alkyl-group:

$$C_6H_5 \cdot NH_2 + CH_3I = C_6H_5 \cdot NH(CH_3) \cdot HI.$$

Secondary and tertiary bases and also quaternary ammonium bases, such as $C_6H_5 \cdot N(CH_3)_3 \cdot OH$, are known. The last are as strongly basic as the corresponding true aliphatic compounds.

The *anilides* are derivatives of aniline, $C_6H_5 \cdot NH_2$, and its homologues: they are acid amides, in which one amino-hydrogen atom has been replaced by a phenyl-group. *Acetoanilide*, $C_6H_5 \cdot NH \cdot COCH_3$, employed as a febrifuge under the name "antifebrine," is a type of these compounds. The anilides are produced by boiling aniline with the corresponding acid. Acetoanilide is obtained by heating aniline with glacial acetic acid:

$$C_6H_5 \cdot NH\boxed{H + HO}OC \cdot CH_3 = C_6H_5 \cdot NH \cdot COCH_3 + H_2O.$$

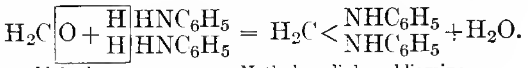
MENSCHUTKIN found that the velocity of formation of acetoanilide is much less for an excess of aniline than for an excess of glacial acetic acid, although on theoretical grounds the velocity of formation should be the same in both cases; for at each moment it should be proportional to the product of the concentrations of the glacial acetic acid (c) and of the aniline (c'), being therefore expressed by

$$s = k \cdot cc',$$

in which k is constant.

The difference between theory and experiment admits of various explanations: one is that the reaction in the two cases takes place in different media. The important influence of the medium is mentioned in **71**.

Aldehydes react with aromatic amines with elimination of water:



$$H_2C\boxed{O+\begin{matrix}H\\H\end{matrix}}\begin{matrix}HNC_6H_5\\HNC_6H_5\end{matrix} = H_2C<\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}+H_2O.$$

Formaldehyde Methylenediphenyldiamine

Primary aromatic amines show the carbylamine-reaction: with nitrous acid they yield diazonium compounds (**339**).

Aniline.

313. Aniline was first obtained by the dry distillation of indigo (Spanish, *anil*): hence its name. It is manufactured by the action of hydrochloric acid and iron-filings on nitrobenzene contained in a cast-iron cylinder fitted with a stirring apparatus:

$$C_6H_5NO_2+3Fe+6HCl = C_6H_5NH_2+2H_2O+3FeCl_2.$$

It is remarkable that in this process only about one-fortieth of the hydrochloric acid required by the equation is needed for the reduction. This is probably because iron-filings and water are able to effect the reduction in presence of ferrous chloride. Lime is added as soon as the reduction is complete, and the aniline is distilled with steam.

Aniline is also obtained by the electro-reduction of nitrobenzene (**326**).

Aniline is a colourless liquid, and, unless perfectly pure, turns brown in the air, the colour-change being probably due to the presence of traces of sulphur compounds. It is only slightly soluble in water: it boils at 183°, and has a specific gravity of 1·024 at 16°. Formaldehyde yields with aniline a remarkable condensation-product, *anhydroformaldehydeaniline*, $(C_6H_5N{=}CH_2)_3$. This substance melts at 40°, and dissolves with difficulty. It is employed in the identification of both formaldehyde and aniline (**117**). Aniline can be reconverted into nitrobenzene by certain oxidizing agents: various intermediate products, such as nitrosobenzene, $C_6H_5{\cdot}NO$, are formed. Aniline somewhat readily undergoes oxidation: the compounds thus produced are described in **321**–**324**.

An aqueous solution of free aniline gives a deep-violet coloration with bleaching-powder solution, the primary product in the reactions being probably *phenylchloroamine*, $C_6H_5 \cdot NHCl$. An aniline salt in acid solution is coloured dark-green to black by potassium dichromate. These two reactions, and that with wood (**227**), serve as tests for aniline. The bleaching-powder reaction is particularly delicate.

Aniline is very sensitive towards oxidizing agents, the final product being nitrobenzene. Intermediate between these two substances is formed a series of derivatives, which are also obtained in the inverse order by the reduction of nitrobenzene (**321–327**):

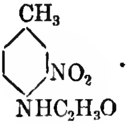
$$\begin{tikzcd}
C_6H_5 \cdot NH_2 \arrow[r] & \underset{\text{Phenylhydroxylamine}}{C_6H_5 \cdot NHOH} \arrow[r] \arrow[d] & \underset{\text{Nitrosobenzene}}{C_6H_5 \cdot NO} \arrow[r] & C_6H_5 \cdot NO_2; \\
 & \underset{p\text{-Aminophenol}}{HO \cdot C_6H_4 \cdot NH_2} \arrow[r] & \underset{\text{Benzoquinone}}{C_6H_4O_2.} &
\end{tikzcd}$$

Since these oxidation-products react with each other and with aniline, yielding substances which undergo further oxidation, numerous, often very complex, derivatives are produced.

Homologues of Aniline.

314. Ortho-*toluidine* and para-*toluidine*, $CH_3 \cdot C_6H_4 \cdot NH_2$, are formed by the reduction of the corresponding nitro-compounds. The *ortho*-compound is a liquid, B.P. 199·4°; the *para*-compound is a solid, M.P. 42·5° The different solubilities of their oxalic-acid salts afford a means of separating them.

m-*Toluidine* can only be obtained indirectly. *p*-Toluidine is converted into its acetyl-derivative, $CH_3 \cdot C_6H_4 \cdot NHC_2H_3O$, which on nitration yields



The acetyl-group in this compound is split off by boiling with hydrochloric acid, after which the amino-group is eliminated by the method described in **341**, 3. On reduction, the *m*-nitrotoluene thus formed yields *m*-toluidine.

The monoamino-derivatives of the xylenes are called *xylidines*. Six isomerides are possible, due to differences in the relative positions of the methyl-groups and the amino-group in the ring. Some of the toluidines and the xylidines are employed in making coal-tar colours, and are, therefore, manufactured in large quantities.

Secondary Amines.

315. *Diphenylamine*, $C_6H_5{\cdot}NH{\cdot}C_6H_5$, melts at 54°, and boils at 310°. It is a type of the true secondary aromatic amines. They are formed by heating the hydrochlorides of the primary amines with the free amines:

$$C_6H_5\boxed{NH_2{\cdot}HCl + H}HN{\cdot}C_6H_5 = NH_4Cl + HN(C_6H_5)_2.$$

Diphenylamine can also be obtained by the action of bromobenzene on potassium anilide, $C_6H_5{\cdot}NHK$.

Diphenylamine has an agreeable, floral odour.

Diphenylamine is a very sensitive reagent for the detection of nitric acid, which produces a deep-blue colour with its solution in concentrated sulphuric acid. This reaction can only be applied to the detection of nitric acid in the absence of other oxidizing substances, such as bromine-water, permanganate, etc., since diphenylamine also gives a blue coloration with many of these reagents.

The method of formation of the mixed aromatic-aliphatic amines, such as *methylaniline*, $C_6H_5{\cdot}NH{\cdot}CH_3$, is indicated in **312**. The action of the alkyl iodide upon aniline results in the substitution of more than one hydrogen atom of the amino-group by an alkyl-group, so that a mixture of the unchanged primary and the secondary and tertiary amines is formed. The secondary amine is obtained pure by first replacing one hydrogen atom of the amino-group by an acid-radical, such as acetyl, and subsequently treating the acetyl-derivative with an alkyl iodide.

To prepare such a compound as methylaniline, for example, aniline is first converted into acetoanilide, $C_6H_5{\cdot}NH{\cdot}COCH_3$, by boiling with glacial acetic acid. The hydrogen atom linked to nitrogen in this compound can be replaced by sodium, yielding $C_6H_5{\cdot}NNa{\cdot}COCH_3$, which on treatment with methyl iodide yields *methylacetoanilide*, $C_6H_5 \cdot N(CH_3).COCH_3$. Saponification with alkalis converts this compound into monomethylaniline.

The secondary aromatic amines, like those of the aliphatic series, are readily converted by nitrous acid into nitrosoamines, such as *nitrosomethylaniline*, $C_6H_5 \cdot N < {NO \atop CH_3}$. On careful reduction, these nitroso-compounds yield *hydrazines*, $C_6H_5 \cdot N < {NH_2 \atop R}$; on energetic reduction, for example with tin and hydrochloric acid, the NO-group is eliminated, and the secondary amines regenerated.

Tertiary Amines.

316. *Triphenylamine*, $(C_6H_5)_3N$, is a type of the true aromatic tertiary amines: only a few of them are known. It is obtained by the action of sodium and bromobenzene on diphenylamine, and is a solid, melting at 127°. It does not possess a basic character.

Dimethylaniline, $C_6H_5 \cdot N < {CH_3 \atop CH_3}$, is the most important member of the series of mixed aromatic-aliphatic tertiary amines. They can be obtained by the action of alkyl halides upon anilines, but are manufactured by heating aniline hydrochloride with the alcohol, a method in which alkyl halides react in the nascent state. Methyl alcohol and hydrochloric acid yield methyl chloride, and this compound then reacts with the aniline.

On heating the hydrochloride of an alkyl-aniline at 180°, in a current of hydrochloric-acid gas, the alkyl-groups are eliminated, with formation of aniline and alkyl chlorides. When the hydrochlorides of the alkyl-anilines are strongly heated, the alkyl-groups linked to nitrogen are transferred to the benzene-ring. This reaction can be explained by assuming that decomposition into alkyl chloride and aniline first takes place as just described:

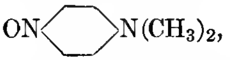
$$\text{I. } C_6H_5 \cdot NH(C_2H_5)HCl = C_6H_5 \cdot NH_2 + C_2H_5Cl.$$

The reaction indicated in equation II. ensues:

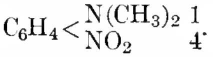
$$\text{II. } C_6H_5 \cdot NH_2 + C_2H_5Cl = C_6H_4 < {C_2H_5 \atop NH_2HCl}.$$

The formation of the hydrochloride of *p*-toluidine, by the interaction of methyl alcohol and aniline hydrochloride at a high temperature, is analogous. By this process it is possible to obtain even *pentamethylaminobenzene*, $C_6(CH_3)_5\cdot NH_2$.

The *para*-hydrogen atoms of dimethylaniline and other dialkylanilines are replaceable by various groups. Thus, dimethylaniline reacts readily with nitrous acid, with formation of *nitrosodimethylaniline*,

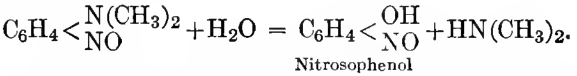


effected by the addition of potassium nitrite to the solution of the tertiary base in hydrochloric acid. This nitroso-compound crystallizes in well-defined leaves of a fine green colour. It melts at 85°, and yields a hydrochloride crystallizing in yellow needles. On oxidation with potassium permanganate, the nitroso-group is converted into a nitro-group, with formation of p-*nitrodimethylaniline*,



$$C_6H_4<\begin{matrix}N(CH_3)_2 & 1\\ NO_2 & 4\end{matrix}.$$

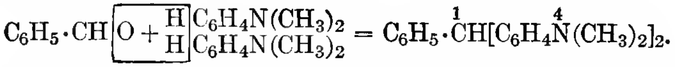
On boiling with caustic soda, the amino-group of nitrosodimethylaniline is removed, with formation of dimethylamine and nitrosophenol:



$$C_6H_4<\begin{matrix}N(CH_3)_2\\ NO\end{matrix}+H_2O = \underset{\text{Nitrosophenol}}{C_6H_4<\begin{matrix}OH\\ NO\end{matrix}}+HN(CH_3)_2.$$

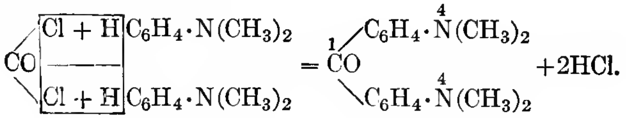
This reaction is employed in the preparation of pure dimethylamine (73).

The *para*-hydrogen atom of dimethylaniline can react with substances other than nitrous acid: thus, aldehydes readily yield a condensation-product:



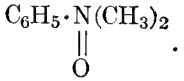
$$C_6H_5\cdot CH\boxed{O+\begin{matrix}H\\ H\end{matrix}}\begin{matrix}C_6H_4N(CH_3)_2\\ C_6H_4N(CH_3)_2\end{matrix} = C_6H_5\cdot\overset{1}{C}H[C_6H_4\overset{4}{N}(CH_3)_2]_2.$$

The constitution of this compound is inferred from its relation to *triphenylmethane*, $CH(C_6H_5)_3$ (423). With dimethylaniline, carbonyl chloride yields a *p*-derivative of benzophenone, $C_6H_5\cdot CO\cdot C_6H_5$, called Michler's ketone:



$$CO\begin{matrix}\diagup\boxed{Cl+H}\,C_6H_4\cdot N(CH_3)_2\\ \diagdown\boxed{Cl+H}\,C_6H_4\cdot N(CH_3)_2\end{matrix} = \overset{1}{C}O\begin{matrix}\diagup C_6H_4\cdot\overset{4}{N}(CH_3)_2\\ \diagdown C_6H_4\cdot\overset{4}{N}(CH_3)_2\end{matrix}+2HCl.$$

When dimethylaniline, and other analogous tertiary amines, are treated with hydrogen peroxide at 60°–70°, they yield compounds such as *dimethylaniline oxide,*



$$\begin{matrix} C_6H_5\cdot N(CH_3)_2 \\ \| \\ O \end{matrix}.$$

The constitution is indicated by its reduction to dimethylaniline.

Quaternary Bases.

317. Quaternary bases are formed by the addition of alkyl halides to the tertiary aromatic-aliphatic amines, and treatment of the salts thus formed with moist silver oxide. These substances are strong bases. On heating, they yield an alcohol and a tertiary amine, differing in this respect from the aliphatic ammonium bases (**73**).

Pope has resolved quaternary ammonium bases containing four dissimilar groups into optically active components. These compounds of the type $NR_1R_2R_3R_4X$, in which X is an acid-radical, owe their optical activity to the presence of an *asymmetric nitrogen atom. Methylallylphenylbenzylammonium hydroxide,*

$$HO\cdot N(CH_3)(C_3H_5)(C_6H_5)(CH_2C_6H_5),$$

unites with the strongly optically active *d*-camphorsulphonic acid: the salt obtained is fractionally crystallized from acetone, a solvent less liable to decompose it than those containing a hydroxyl-group. By this means the base can be resolved into its dextro-rotatory and lævo-rotatory components. A complete demonstration of the position and direction of the bonds of the quinquivalent nitrogen atom has not yet been given.

Benzylamine, $C_6H_5\cdot CH_2\cdot NH_2$.

318. *Benzylamine* is a type of the amines with NH_2 in the side-chain. It can be obtained by the various methods employed in the preparation of aliphatic amines, such as the action of benzyl chloride upon ammonia, by which *dibenzylamine* and *tribenzylamine* are also formed; addition of hydrogen to benzonitrile, $C_6H_5\cdot CN$; reduction of phenylnitromethane, $C_6H_5\cdot CH_2\cdot NO_2$; and so on. The method for its formation and its properties prove that benzylamine belongs to the primary amines of the aliphatic series: thus, it does not yield diazonium compounds; and its aqueous solution has a strongly alkaline reaction, proving it to be a much stronger base than aniline, in which the NH_2-group is under the direct influence of the phenyl-group.

Benzylamine is a liquid of ammoniacal odour: it boils at 185°, is volatile with steam, and has a specific gravity of 0·983 at 19°. It absorbs carbon dioxide from the air.

Derivatives of Aniline and Carbonic Acid.

319. Only a few of the numerous compounds of aniline with carbonic acid can be described here. *Phenylurethane,*

$$C_6H_5 \cdot NH \cdot CO \cdot OC_2H_5,$$

is formed by the interaction of ethyl chlorocarbonate and aniline. It is a solid, and melts at 52°. When distilled with phosphoric oxide, it yields *phenyl isocyanate*, $C_6H_5 \cdot N:C:O$, a colourless liquid productive of tears, which boils at 166°. It is sometimes employed in the detection of OH-groups or NH_2-groups, with which it forms substituted urethanes and ureas respectively. With water it yields symmetrical *diphenylurea*, $CO(NH \cdot C_6H_5)_2$, a crystalline substance melting at 235° (273)

Derivatives of Aniline and Sulphur.

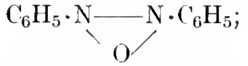
320. Derivatives of aniline and sulphur, similar to the compounds described in 265 and 275, are also known. One of them is *phenyl mustard-oil*, $C_6H_5 \cdot N:C:S$, which boils at 222°. It is obtained by boiling *diphenylthiourea*, $CS(NH \cdot C_6H_5)_2$, with hydrochloric acid. Diphenylthiourea itself is formed by heating carbon disulphide with aniline:

$$CS_2 + 2H_2N \cdot C_6H_5 = H_2S + CS(NH \cdot C_6H_5)_2.$$

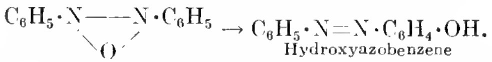
VIII. INTERMEDIATE PRODUCTS IN THE REDUCTION OF AROMATIC NITRO-COMPOUNDS.

321. On reduction, the nitro-compounds of the aliphatic series yield amines directly, from which the alkyl-groups can be removed by oxidation: for example, ethylamine is converted into acetic acid and ammonia. In the aromatic series, on the other hand, intermediate products can be obtained in the reduction of nitro-compounds, and sometimes also in the oxidation of amines. Only the compounds derived from nitrobenzene and aniline will be described here, although numerous substitution-products of the same type are known.

In acid solution the nitro-compounds are directly reduced to the corresponding amino-derivatives, but in alkaline solution yield substances containing two benzene-residues. Nitrobenzene yields in succession *azoxybenzene*, *azobenzene*, *hydrazobenzene*, and aniline:

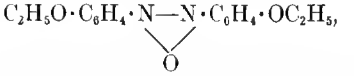
1. Nitro-compound,	$C_6H_5 \cdot NO_2 \quad O_2N \cdot C_6H_5$;
2. *Azoxy-compound,*	 $C_6H_5 \cdot N \text{——} N \cdot C_6H_5$; $\underset{O}{\diagdown\diagup}$
3. *Azo-compound,*	$C_6H_5 \cdot N{=}N \cdot C_6H_5$;
4. *Hydrazo-compound,*	$C_6H_5 \cdot NH{-}NH \cdot C_6H_5$;
5. Amino-compound,	$C_6H_5 \cdot NH_2 \quad H_2N \cdot C_6H_5$.

322. *Azoxybenzene* is obtained by boiling nitrobenzene with alcoholic potash, and is also formed in the oxidation of aniline with potassium permanganate in alcoholic solution. It forms light-yellow crystals melting at 36° When warmed with concentrated sulphuric acid, it is transformed into p-*hydroxyazobenzene:*



$$C_6H_5 \cdot N \text{——} N \cdot C_6H_5 \;(\underset{O}{\diagdown\diagup}) \longrightarrow \underset{\text{Hydroxyazobenzene}}{C_6H_5 \cdot N{=}N \cdot C_6H_4 \cdot OH}.$$

It is readily attacked by various reducing agents. Under the influence of direct sunlight, concentrated sulphuric acid converts azoxybenzene into o-*hydroxyazobenzene.*

323. p-*Azoxyphenetole,*  $C_2H_5O \cdot C_6H_4 \cdot N{-}N \cdot C_6H_4 \cdot OC_2H_5$ ($\underset{O}{\diagdown\diagup}$), is distinguished by its power of forming *liquid crystals,* a property characteristic of a considerable number of other substances. When heated, it melts at 134° to a turbid liquid, which suddenly becomes clear at 165° The crystalline structure of the turbid liquid cannot be detected by the microscope, but is indicated by the double refraction exhibited by the liquid, and by the formation of the figures characteristic of double-refracting crystals between crossed Nicol prisms in converging light.

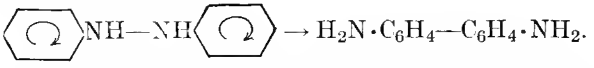
Turbidity is not an essential characteristic of liquid crystals, as VORLÄNDER has discovered perfectly clear liquids which display phenomena like those of double-refracting crystals.

324. *Azobenzene,* $C_6H_5 \cdot N{:}N \cdot C_6H_5$, is formed by the reduction of nitrobenzene with a solution of stannous chloride in excess of caustic potash, and also by distilling azoxybenzene with iron-filings. It is produced along with azoxybenzene by the oxidation of aniline with potassium permanganate.

Azobenzene forms well-defined, orange-red crystals, melting at 68°, and boiling without decomposition at 295°. It is a very stable compound, and is insoluble in water. Its constitution follows from its yielding aniline on reduction.

Hydrazobenzene, $C_6H_5 \cdot NH—NH \cdot C_6H_5$, is formed by the action of zinc-dust and alcoholic potash upon azobenzene or nitrobenzene. It is a colourless, crystalline substance, and melts at 126°. Strong reducing agents convert it into aniline: on the other hand, it is readily oxidized to azobenzene, the transformation being slowly effected by atmosphere oxygen. It is also oxidized to the azo-compound by ferric chloride.

The most characteristic reaction of hydrazobenzene is its conversion into *benzidine*, whereby the benzene-nuclei are, as it were, turned end for end. This "benzidine-transformation" is effected by the action of strong acids:

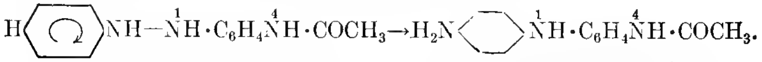


Hydrazobenzene Benzidine

That a diaminodiphenyl is thus formed is proved by the conversion of benzidine into diphenyl, $C_6H_5 \cdot C_6H_5$. The amino-groups occupy the *para*-positions:

By reducing azobenzene in acid solution, benzidine is formed directly. It is characterized by the sparing solubility in cold water of its sulphate.

The amino-groups in benzidine are proved in various ways to occupy the *para*-position: for example, a hydrazobenzene the *p*-hydrogen atoms of which have been substituted cannot be converted into benzidine. In certain instances compounds of this kind can undergo a remarkable intramolecular transformation, known as the "semidine-transformation," forming derivatives of diphenylamine by the turning of only one of the benzene-nuclei:



p-Acetaminohydrazobenzene *p*-Aminophenyl-*p*-acetamino-phenylamine

Electro-reduction of Nitro-compounds.

325. There is reason to believe that in the future electrolytic methods will be used more and more in chemical work, for the electric current affords a means of varying the pressure and concentration of the substances taking part in reactions in the preparation of organic compounds, which is not otherwise attainable. By its aid it is possible to effect new syntheses or to improve those already

known. An explanation of this mode of altering the pressure and concentration is necessary here.

Alteration in the contact-difference of potential between the electrodes and the electrolyte causes considerable variation in the pressure at which the discharged ions leave the solution (280). In reduction-processes the same effect is attained by using different reducing agents. When a compound yields a series of intermediate products on treatment with different reducing agents of increasing strength, this can also be effected by increasing the contact-difference of potential (280) at the cathode, where hydrogen is evolved.

Regarding variation in the concentration, it must be remembered that the electrolytic process takes place only in the immediate neighbourhood of the electrodes. When the surface-area of the electrodes is altered, the strength of the current remaining the same, the number of ions discharged at unit surface varies in direct proportion: it is therefore possible, by selecting suitable electrodes, to cause the concentration of the ions discharged at them to vary within wide limits. The "strength" of the reducing agent depends upon the contact-difference of potential, but its concentration is controlled by the density of the current (168). In reactions in which the discharged ions must interact, as in the synthesis of dibasic acids (*loc. cit.*), a current of high density is necessary: on the other hand, in reductions which must take place as far as possible at all parts of the liquid, large cathodes, which give a current of small density, must be used.

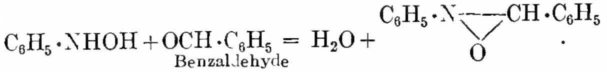
326. On reduction, nitro-compounds ultimately yield amines, but a number of intermediate reduction-products can be isolated. For this reason the electro-reduction of nitrobenzene and its derivatives is of both theoretical and practical importance. It is possible to give a complete and satisfactory explanation of the mechanism of this process.

A distinction must be drawn between primary or electrolytic, and secondary or chemical, reduction-products. The primary process is

$$\underset{\text{Nitrobenzene}}{C_6H_5\cdot NO_2} \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5\cdot NO} \rightarrow \underset{\substack{\text{Phenylhydroxyl-}\\\text{amine}}}{C_6H_5\cdot NHOH} \rightarrow \underset{\text{Aniline}}{C_6H_5\cdot NH_2}.$$

The presence of nitrosobenzene can be detected by the addition of hydroxylamine to the liquid, with which it reacts with loss of one molecule of water, and formation of diazonium hydroxide, $C_6H_5\cdot N_2\cdot OH$: on adding α-naphthol, an azo-dye is produced (361).

The formation of phenylhydroxylamine can be proved by adding benzaldehyde, with which it yields *benzylidenephenylhydroxylamine:*



$$\underset{\text{Benzaldehyde}}{C_6H_5\cdot NHOH + OCH\cdot C_6H_5} = H_2O + \underset{O}{C_6H_5\cdot N\diagdown\!\!-\!\!-\!\!\diagup CH\cdot C_6H_5}.$$

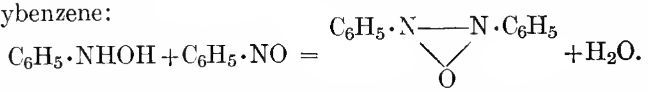
On rapid reduction of nitrobenzene dissolved in moderately concentrated sulphuric acid, with addition of alcohol to increase the solubility, the primary process just described takes place, about 90 per cent. of the theoretical yield of aniline being obtained. In a strongly acid solution, however, the *phenylhydroxylamine* is very quickly converted into p-*aminophenol:*

$$C_6H_5\cdot NHOH \rightarrow HO\cdot C_6H_4\cdot NH_2.$$

This substance is not further reduced. Since phenylhydroxylamine undergoes the same transformation, though much more slowly, in presence of more dilute acid, it is evident that the theoretical yield of aniline cannot be obtained, even when the solvent is dilute, and the velocity of reduction great.

In alcoholic-alkaline solution the electro-reduction of nitrobenzene is accompanied by two secondary processes.

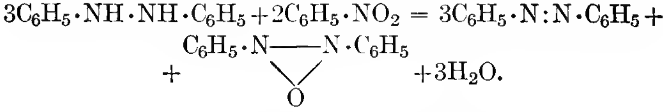
1. Nitrosobenzene reacts with phenylhydroxylamine, yielding azoxybenzene:



$$C_6H_5\cdot NHOH + C_6H_5\cdot NO = \underset{O}{C_6H_5\cdot N\diagdown\!\!-\!\!-\!\!\diagup N\cdot C_6H_5} + H_2O.$$

In presence of alkali this reaction proceeds much more quickly than the further reduction of phenylhydroxylamine, so that only small quantities of aniline are formed, and higher reduction-products of azoxybenzene, chief among them hydrazobenzene, obtained as the main part of the yield.

2. Hydrazobenzene is attacked by the unreduced nitrobenzene with formation of azobenzene and azoxybenzene:



$$3C_6H_5\cdot NH\cdot NH\cdot C_6H_5 + 2C_6H_5\cdot NO_2 = 3C_6H_5\cdot N:N\cdot C_6H_5 + \underset{O}{C_6H_5\cdot N\diagdown\!\!-\!\!-\!\!\diagup N\cdot C_6H_5} + 3H_2O.$$

Since hydrazobenzene in alkaline solution is quickly oxidized by atmospheric oxygen to azobenzene, the yield of azobenzene is very good.

A much higher contact-difference of potential at the cathode is required to reduce hydrazobenzene to aniline.

327. **Haber** has combined these primary and secondary reactions in the following scheme, the vertical arrows indicating primary, and the oblique arrows secondary, reactions:

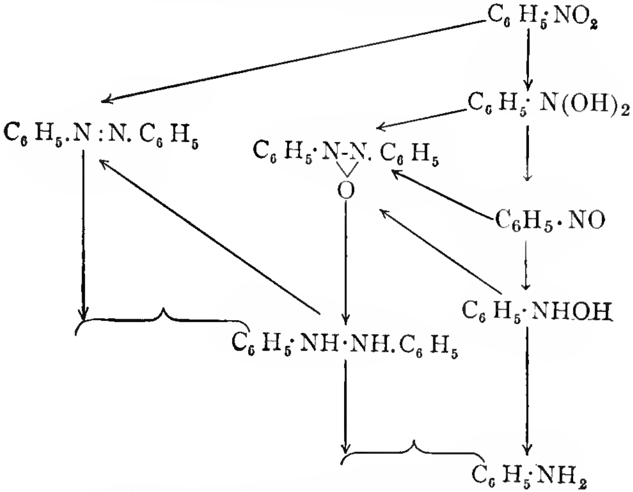


Fig. 77.—Haber's Electro-reduction Scheme.

Bamberger pointed out that the reduction of nitrobenzene by purely chemical methods yields the same intermediate products. Thus, nitrosobenzene is formed by its interaction with zinc-dust and water. In accord with this view is the fact that the velocity of reduction of nitrobenzene by stannous chloride in presence of a great excess of hydrochloric-acid solution indicates that the reaction is bimolecular, and must therefore be represented by the equation

$$R\cdot NO_2+SnCl_2+nHCl = R\cdot NO+SnCl_4+H_2O+(n-2)HCl.$$

This reaction has a measurable velocity. The further reduction of the nitroso-compound to the amino-compound should be very rapid: experimental evidence confirming this theoretical view is afforded by the fact that when nitrosodimethylaniline is brought into contact with stannous chloride, it is at once reduced.

IX. PHENYL-COMPOUNDS CONTAINING OTHER ELEMENTS.

Phosphorus and Arsenic Derivatives.

328. Compounds of phosphorus and arsenic with aromatic hydrocarbons, having constitutions similar to those of the nitro-compounds, azo-compounds, and amino-compounds, are known.

Phosphinobenzene, $C_6H_5\cdot PO_2$, cannot be obtained analogously to nitrobenzene, by the interaction of metaphosphoric acid and benzene. It is prepared by the action of *phenylphosphinic acid* (79) upon its chloride:

$$\underset{\text{Phenylphosphinic acid}}{C_6H_5\cdot PO(OH)_2} + \underset{\text{Chloride}}{C_6H_5\cdot POCl_2} = 2C_6H_5\cdot PO_2 + 2HCl.$$

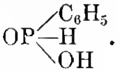
It is a white, crystalline, odourless powder.

Phenylphosphine, $C_6H_5\cdot PH_2$, is obtained by distilling *phosphenyl chloride,* $C_6H_5\cdot PCl_2$, with alcohol, in a current of carbon dioxide. It is a liquid of very penetrating odour. It cannot be obtained by the reduction of phosphinobenzene.

Phosphobenzene, $C_6H_5\cdot P:P\cdot C_6H_5$, is got by treating phenylphosphine with phosphenyl chloride:

$$C_6H_5\cdot P\boxed{Cl_2+H_2}P\cdot C_6H_5 = C_6H_5\cdot P:P\cdot C_6H_5 + 2HCl.$$

It is a pale-yellow powder, insoluble in water, alcohol, and ether. It is energetically oxidized by weak nitric acid, forming *phosphenylous acid,*



$$OP\begin{cases}C_6H_5\\H\\OH\end{cases}.$$

Phosphenyl chloride, $C_6H_5\cdot PCl_2$, the starting-point in the preparation of these and other aromatic phosphorus derivatives, can be prepared, as can its homologues, by heating aromatic hydrocarbons with phosphorus trichloride and aluminium chloride under a reflux-condenser.

Arsinobenzene, $C_6H_5\cdot AsO_2$, is obtained by the elimination of water from *phenylarsonic acid,* $C_6H_5\cdot AsO(OH)_2$, under the influence of heat.

Arsenobenzene, $C_6H_5\cdot As:As\cdot C_6H_5$, is formed by the reduction of *phenylarsine oxide,* $C_6H_5\cdot AsO$, with phosphorous acid. It forms yellow needles, and is converted by oxidation into phenylarsonic acid, $C_6H_5\cdot AsO(OH)_2$. "Atoxyl," employed in the treatment of trypanosomiasis (sleeping sickness), is the sodium salt of *p-aminophenylarsonic acid,* $NH_2\cdot C_6H_4\cdot AsO(OH)_2$.

Comparison of the Aromatic Derivatives of Nitrogen, Phosphorus, and Arsenic.

329. The following compounds are known:

$C_6H_5\cdot NO_2$ Nitrobenzene	$C_6H_5\cdot N_2\cdot C_6H_5$ Azobenzene	$C_6H_5\cdot NH_2$ Phenylamine
$C_6H_5\cdot PO_2$ Phosphinobenzene	$C_6H_5\cdot P_2\cdot C_6H_5$ Phosphobenzene	$C_6H_5\cdot PH_2$ Phenylphosphine
$C_6H_5\cdot AsO_2$ Arsinobenzene	$C_6H_5\cdot As_2\cdot C_6H_5$ Arsenobenzene	

Substances in the first column may be regarded as derived from the *meta*-acids, $HO \cdot NO_2$, $HO \cdot PO_2$, $HO \cdot AsO_2$ by exchange of hydroxyl for phenyl, and hence cannot have acidic properties. Orthonitric acid, H_3NO_4, or $ON(OH)_3$, corresponding to orthophosphoric acid, H_3PO_4 and orthoarsenic acid, H_3AsO_4, is not known, and accordingly nitrobenzene does not unite with water, while phosphinobenzene and arsinobenzene produce the corresponding acids, phenylphosphinic acid, $C_6H_5 \cdot PO(OH)_2$, and phenylarsonic acid, $C_6H_5 \cdot AsO(OH)_2$. When heated, phosphoric acid does not yield phosphorus pentoxide; arsenic acid yields arsenic pentoxide. Similarly, phosphinobenzene cannot be obtained by heating phenylphosphinic acid, while phenylarsonic acid is converted into arsinobenzene by this treatment.

The methods of formation of the compounds of the second column also differ greatly from one another. They are all coloured, the most deeply tinted being azobenzene. On reduction, nitrobenzene and arsinobenzene yield azobenzene and arsenobenzene: the oxygen of phosphinobenzene is too firmly linked to phosphorus to admit of this reaction. Hydrogen reduces azobenzene to phenylamine: chlorine converts phosphobenzene and arsenobenzene into the corresponding chlorine derivatives, $C_6H_5 \cdot PCl_2$ and $C_6H_5 \cdot AsCl_2$.

The difference between the two compounds in the last column is due to the strong affinity of phosphorus for oxygen. Aniline cannot be oxidized to an acid, while phenylphosphine is readily converted, even by the oxygen of the atmosphere, into *phenylphosphinous acid*, $C_6H_5 \cdot PO_2H_2$.

Aromatic Metallic Compounds.

330. Mercury, tin, lead, and magnesium are the only metals which yield aromatic compounds: they are much less important than the metallic compounds of the aliphatic series. *Mercury phenide*, $Hg(C_6H_5)_2$, is obtained by the action of sodium-amalgam upon bromobenzene. It is crystalline, and resembles the corresponding alkyl-derivatives in its stability towards atmospheric oxygen. When its vapour is passed through a red-hot tube, it decomposes into mercury and diphenyl (420): the same effect is partially produced by distillation. When mercury acetate is heated with benzene at 110°, there results *phenylmercury acetate*, $C_6H_5 \cdot Hg \cdot OOC \cdot CH_3$, the acetic-acid salt of the base *phenylmercury hydroxide*, $C_6H_5 \cdot Hg \cdot OH$. The homologues of benzene, nitrobenzene, and other substances yield analogous compounds.

Aromatic magnesium compounds are referred to in 298.

BENZOÏC ACID: ITS DERIVATIVES AND HOMOLOGUES.

Benzoïc Acid, $C_6H_5\cdot COOH$.

331. *Benzoïc acid* can be prepared by many methods, of which the most important will be described.

1. By the oxidation of any aromatic hydrocarbon with a side-chain:

$$C_6H_5\cdot C_nH_{2n+1} \rightarrow C_6H_5\cdot COOH.$$

Being inexpensive, toluene is specially serviceable for this purpose. In the manufacture of benzoïc acid, toluene is not directly oxidized, but is treated at its boiling-point with chlorine. *Benzotrichloride*, $C_6H_5\cdot CCl_3$, is first formed, and is converted into benzoïc acid by heating with water:

$$C_6H_5\cdot C\boxed{\begin{array}{l}Cl\quad H\\ Cl+H\\ Cl\quad H\end{array}}\begin{array}{l}OH\\ OH-H_2O = C_6H_5\cdot COOH+3HCl.\\ OH\end{array}$$

Benzoïc acid thus prepared often contains traces of *chlorobenzoïc acid*, $C_6H_4Cl\cdot COOH$.

2. By the oxidation of aromatic alcohols or aldehydes, such as benzyl alcohol, $C_6H_5\cdot CH_2OH$, or benzaldehyde, $C_6H_5C{<}{}^{H}_{O}$: also by the oxidation of alcohols, aldehydes, or ketones with longer side-chains: in fact, from all compounds containing a side-chain with one carbon atom directly linked to the benzene-nucleus.

3. By the introduction of the nitrile-group into the benzene-nucleus, and hydrolysis of the *benzonitrile*, $C_6H_5\cdot CN$, thus formed. The introduction of the nitrile-group can be effected in two ways.

(*a*) By diazotizing aniline, and treating the diazonium salt with potassium cyanide (**341**, 5).

(*b*) By distilling potassium benzenesulphonate with potassium cyanide:

$$C_6H_5\cdot SO_3K + KCN = C_6H_5\cdot CN + K_2SO_3.$$

4. By the action of carbon dioxide and sodium on bromobenzene, whereby sodium benzoate is formed:

$$C_6H_5Br + CO_2 + 2Na = NaBr + C_6H_5\cdot CO_2Na.$$

5. By the action of various derivatives of carbonic acid, other than carbon dioxide, upon benzene, substances readily convertible into benzoïc acid are formed.

(*a*) In presence of aluminium chloride, benzene and carbonyl chloride react together, with formation of *benzoyl chloride*, the chloride of benzoïc acid, and hydrochloric acid:

$$C_6H_5\boxed{H + Cl}\cdot COCl = \underset{\text{Benzoyl chloride}}{C_6H_5\cdot COCl} + HCl.$$

Benzoyl chloride is converted into benzoïc acid by treatment with hot water.

(*b*) Benzene and aluminium chloride react with *carbamic chloride*, $Cl\cdot CONH_2$ (formed by passing carbonyl chloride over heated ammonium chloride), yielding *benzamide*, the amide of benzoïc acid:

$$C_6H_5\boxed{H + Cl}\cdot CONH_2 = \underset{\text{Benzamide}}{C_6H_5\cdot CONH_2} + HCl.$$

(*c*) Bromobenzene is converted by sodium and ethyl chlorocarbonate into *ethyl benzoate:*

$$\begin{array}{r|l|l} C_6H_5 & Br + Cl & \cdot COOC_2H_5 \\ + & Na \quad Na & \\ \cline{2-2} \end{array} = C_6H_5\cdot COOC_2H_5 + NaCl + NaBr.$$

Benzoïc acid is a constituent of many natural resins and balsams, such as gum-benzoïn, Peru-balsam, and Tolu-balsam. A derivative, hippuric acid (230), is present in the urine of horses. It was formerly prepared principally from gum-benzoïn, from which source the benzoïc acid used as a medicament is still sometimes obtained. It is a white solid, crystallizing in leaf-like crystals melting at 121·4°. It sublimes readily, and boils at 250°: it volatilizes with steam, and can be purified by steam-distillation. Its alkali-metal salts dissolve readily in water, most salts of other bases being soluble with difficulty.

332. The solubility-curve ("Inorganic Chemistry," 235) of benzoïc acid has been the subject of careful investigation, on account of its interesting character (Fig. 78). The solubility increases somewhat rapidly with increase of temperature up to 90° (*AB*). At this temperature, the acid melts beneath the water, so that two liquids result: one is an aqueous solution, containing 11·2 per cent. of acid (point *B*); the other consists principally of the acid, containing 95·88 per cent. (point *D*). Above this temperature an effect like that described in 74 is produced: the mutual solubility of these layers is represented in the part *BCD* of the curve, of which *BC* corresponds to the aqueous layer, and *DC* to the acid one. The composition of the two layers becomes more and more alike as the temperature rises, since the water dissolves more benzoïc acid, and the acid more water. At 116° they are identical in composition: that is, the liquid has again become homogeneous.

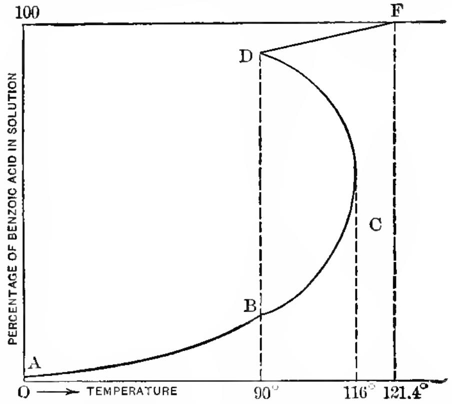
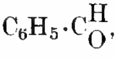


FIG. 78.—SOLUBILITY-CURVE OF BENZOÏC ACID IN WATER.

If more benzoïc acid is added to the acid layer only, at 90°, it is necessary to raise the temperature to keep all the acid fused: the line *DF* is thus obtained, ending at *F* at the melting-point of pure benzoïc acid, 121·4°. *DF* therefore represents the melting-point-curve of the acid, on addition of increasing amounts of water.

Derivatives of Benzoïc Acid.

333. *Benzoyl chloride*, $C_6H_5\cdot COCl$, can be obtained by the action of phosphorus pentachloride or oxychloride upon benzoïc acid, or by the method of **331,** 5*a*. It is a liquid of disagreeable odour, and boils at 194°. It is manufactured by treating benzaldehyde,  $C_6H_5\cdot C\overset{H}{\underset{O}{}}$, with chlorine. Unlike acetyl chloride, which is rapidly decomposed, it is very slowly acted upon by water at ordinary temperatures.

Benzoyl chloride is employed in the introduction of the benzoyl-group, $C_6H_5\cdot CO$—, into compounds. This is effected by a method discovered by Baumann and Schotten, which consists in agitating the substance in alkaline solution with benzoyl chloride.

Thus, *glyceryl tribenzoate* is prepared by addition of small quantities of caustic potash and benzoyl chloride to an aqueous solution of glycerol. The cooled mixture is constantly agitated, and, finally, caustic potash is added until the smell of benzoyl chloride has vanished.

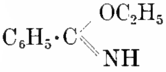
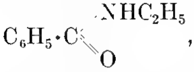
Benzoïc anhydride, $C_6H_5CO\cdot O\cdot COC_6H_5$, is formed by the interaction of a benzoate and benzoyl chloride:

$$C_6H_5\cdot CO\cdot O\boxed{Na + Cl}\cdot OCC_6H_5 = NaCl + C_6H_5CO\cdot O\cdot COC_6H_5.$$

At ordinary temperatures it is very stable towards water, but is decomposed when boiled with it, yielding benzoïc acid.

The formation of *ethyl benzoate* (**331,** 5*c*) is sometimes employed as a test for ethyl alcohol, since it possesses a characteristic peppermint-like odour.

Benzamide (**331,** 5*b*), $C_6H_5\cdot CONH_2$, can be prepared by the action of ammonia or ammonium carbonate on benzoyl chloride. It is crystalline and dimorphous, melting at 130°. It is stated in **104** that the influence of the negative acetyl-group causes the hydrogen atoms of the amino-group in acetamide to be replaceable by metals. Benzamide displays this property to an even greater extent, on account of the more negative character of the benzoyl-group; for the values of the dissociation-constants for acetic acid and for benzoïc acid respectively are $10^4k = 0\cdot18$ and $10^4k = 0\cdot60$.

When the silver compound of benzamide is treated with an alkyl iodide at ordinary temperatures, an O-ether, *benzoïc iminoether*,  $C_6H_5{\cdot}C\begin{matrix}\diagup OC_2H_5\\ \diagdown\!\!\diagdown NH\end{matrix}$, is formed. The constitution of this substance is proved by its yielding ammonia and alcohol, instead of ethylamine and benzoïc acid, when treated with alkalis. When, however, the silver compound is treated with an alkyl iodide at 100°, a *N*-alkide,  $C_6H_5{\cdot}C\begin{matrix}\diagup NHC_2H_5\\ \diagdown\!\!\diagdown O\end{matrix}$, is formed. This is proved by the decomposition of the latter substance into ethylamine and benzoïc acid, so that the silver compound must have different constitutions at ordinary temperatures and at 100° (267).

Benzonitrile, $C_6H_5{\cdot}CN$, the methods of producing which are described in 331, 3, can also be produced similarly to the aliphatic nitriles: for example, by the action of phosphoric oxide upon benzamide. It is a liquid with an odour resembling that of bitter almonds, and boils at 191°. It has all the properties characteristic of the aliphatic nitriles.

Homologues of Benzoïc Acid.

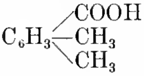
334. The *toluic acids*,  $C_6H_4<^{CH_3}_{COOH}$, are formed by the oxidation of the corresponding xylenes with dilute nitric acid. *p*-Toluic acid is one of the oxidation-products of the turpentine-oils, which are first converted by oxidation into cymene,

The toluic acids are only slightly soluble in cold water.

Phenylacetic acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$, is isomeric with them, and can be obtained by the method indicated in the following scheme:

$$\underset{\text{Benzyl chloride}}{C_6H_5{\cdot}CH_2{\cdot}Cl} + KCN \rightarrow \underset{\text{Benzyl cyanide}}{C_6H_5{\cdot}CH_2{\cdot}CN} \rightarrow C_6H_5{\cdot}CH_2{\cdot}COOH.$$

It is readily distinguished from the toluic acids by oxidation, which converts it into the monobasic benzoïc acid, while the toluic acids yield the dibasic phthalic acids (366).

Xylic acids,  $C_6H_3\begin{matrix}\diagup COOH\\ -CH_3\\ \diagdown CH_3\end{matrix}$, have properties corresponding to those of benzoïc acid: they, too, are only slightly soluble in cold water.

AROMATIC ALDEHYDES AND KETONES.

Aldehydes.

335. *Benzaldehyde*, $C_6H_5\cdot C\genfrac{}{}{0pt}{}{H}{O}$, is the best-known of the aromatic aldehydes. Like the aliphatic aldehydes, it is formed by the oxidation of the corresponding alcohol, benzyl alcohol, $C_6H_5\cdot CH_2OH$, and by distillation of a mixture of a benzoate and a formate. It is manufactured by heating *benzal chloride,* $C_6H_5\cdot CHCl_2$, with water and calcium carbonate, a method the aliphatic analogue of which is of no practical importance:

$$C_6H_5\cdot CH\boxed{Cl_2+\genfrac{}{}{0pt}{}{H}{H}}\genfrac{}{}{0pt}{}{OH}{OH}-H_2O = C_6H_5\cdot C\genfrac{}{}{0pt}{}{H}{O}+2HCl.$$

Benzaldehyde is isolated from the crude reaction-product by treatment with an aqueous solution of sulphur dioxide, in which it dissolves with formation of *benzaldehydesulphurous acid* (**110**, 2), the other substances present being insoluble. When a current of air is passed through the heated solution, the benzaldehyde is obtained pure.

The following methods are employed in the preparation of the homologues of benzaldehyde.

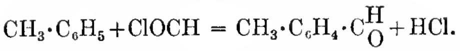
1. When ethyl chloro-oxalate is brought into contact with an aromatic hydrocarbon in presence of aluminium chloride, the ethyl ester of an α-ketonic acid is produced:

$$C_6H_6+\underset{\text{Ethyl chloro-oxalate}}{ClCO—COOC_2H_5} = C_6H_5\cdot CO\cdot COOC_2H_5+HCl.$$

The free acid is obtained by saponification, and on dry distillation loses CO_2, with formation of the aldehyde:

$$C_6H_5\cdot CO\cdot CO_2H = C_6H_5\cdot C\genfrac{}{}{0pt}{}{H}{O}+CO_2.$$

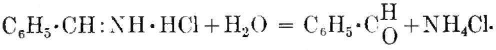
2. An aromatic hydrocarbon is treated with a mixture of carbon monoxide and hydrochloric acid in presence of aluminium chloride and a trace of cuprous chloride. It may be assumed that formyl chloride, HCOCl, is obtained as an intermediate product:



$$CH_3\cdot C_6H_5+ClOCH = CH_3\cdot C_6H_4\cdot C\overset{H}{\underset{O}{}}+HCl.$$

3. When anhydrous hydrocyanic acid and hydrochloric acid are brought into contact with aromatic hydrocarbons, aldehydes are produced, an *aldime* being formed as an intermediate product:

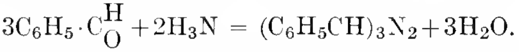
$$C_6H_6+CNH+HCl = \underset{\text{Benzaldime hydrochloride}}{C_6H_5\cdot CH:NH\cdot HCl};$$



$$C_6H_5\cdot CH:NH\cdot HCl+H_2O = C_6H_5\cdot C\overset{H}{\underset{O}{}}+NH_4Cl.$$

Benzaldehyde occurs in the natural product, amygdalin, $C_{20}H_{27}O_{11}N$ (**262**); on this account it is called *oil of bitter almonds*. It is a liquid of agreeable odour, is slightly soluble in water, boils at 179°, and has a specific gravity 1·0504 at 15° It has most of the properties of the aliphatic aldehydes: it is readily oxidized, even by the oxygen of the atmosphere (especially when exposed to sunlight), reduces an ammoniacal silver solution with formation of a mirror, yields a crystalline addition-product with sodium hydrogen sulphite, adds on hydrocyanic acid and hydrogen, forms an oxime and a phenylhydrazone, and so on.

It displays, however, points of difference from the fatty aldehydes. Thus, with ammonia at the ordinary temperature it does not yield a compound like acetaldehyde-ammonia, but produces *hydrobenzamide*, $(C_6H_5CH)_3N_2$, formed by the union of three molecules of benzaldehyde and two molecules of ammonia:



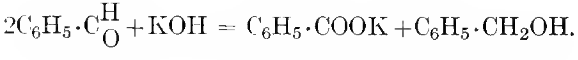
$$3C_6H_5\cdot C\overset{H}{\underset{O}{}}+2H_3N = (C_6H_5CH)_3N_2+3H_2O.$$

At −20°, however, ammonia combines with benzaldehyde to *benzaldehyde-ammonia*, $2C_6H_5\cdot CHO\ NH_3$, probably

$$NH[CH(C_6H_5)\cdot OH]_2,$$

which separates in plates melting at 45°. After a time it decomposes into hydrobenzamide, benzaldehyde, and water. It is an intermediate product in the preparation of hydrobenzamide.

The behaviour of the aromatic aldehydes towards alcoholic potash is characteristic, one molecule of the aldehyde being oxidized, and the other reduced (*cf.*, however, **117**). Thus, benzaldehyde yields potassium benzoate and benzyl alcohol:



$$2C_6H_5\cdot C\overset{H}{\underset{O}{}}+KOH = C_6H_5\cdot COOK+C_6H_5\cdot CH_2OH.$$

The aromatic aldehydes condense readily with dimethylaniline or phenols, forming derivatives of triphenylmethane (**423**):

$$C_6H_5\cdot C\boxed{\begin{matrix}H\\O\end{matrix}+\begin{matrix}H\\H\end{matrix}}\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix} = C_6H_5\cdot CH<\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix}+H_2O.$$

Autoxidation.

It has been observed that during the oxidation of various substances in the air as much oxygen is rendered "active" as is taken up by the substance under oxidation ("Inorganic Chemistry," **161**): this phenomenon is displayed in the atmospheric oxidation of benzaldehyde. If it is left for several weeks in contact with water, indigosulphonic acid, and air, the same amount of oxygen is absorbed in oxidizing the indigo derivative as in converting the benzaldehyde into benzoïc acid. Von Baeyer has shown that benzoyl-hydrogen peroxide, $C_6H_5CO\cdot O\cdot OH$, is formed as an intermediate product, and oxidizes the indigosulphonic acid, being itself reduced to benzoïc acid:

$$C_6H_5\cdot CHO+O_2 = C_6H_5\cdot CO\cdot O\cdot OH;$$

$$C_6H_5\cdot CO\cdot O\cdot OH+\text{Indigo} = C_6H_5\cdot COOH+\text{Oxidized indigo}.$$

The oxidation of benzaldehyde in the air must be considered, therefore, to take place thus:

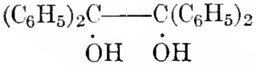
$$C_6H_5\cdot CHO+O_2 = C_6H_5\cdot CO\cdot O\cdot OH;$$
$$C_6H_5\cdot CO\cdot O\cdot OH+C_6H_5\cdot CHO = 2C_6H_5\cdot COOH.$$

Von Baeyer has, in fact, proved that benzoyl-hydrogen peroxide dissolves when added to benzaldehyde, but that the liquid gradually solidifies to pure benzoïc acid.

Ketones.

336. The *aromatic ketones* can be subdivided into the mixed aromatic-aliphatic ketones and the true aromatic ketones. The typical member of the first class is *acetophenone*, $C_6H_5\cdot CO\cdot CH_3$. It can be obtained by distilling a mixture of calcium acetate and benzoate, or more readily by the addition of aluminium chloride to a mixture of benzene and acetyl chloride. It is a crystalline substance of agreeable odour, melting at 20° and boiling at 200°: it is slightly soluble in water, and possesses all the properties of the aliphatic ketones. It is employed as a soporific under the name "hypnone."

Benzophenone, $C_6H_5\cdot CO\cdot C_6H_5$, is a true aromatic ketone, and can be obtained by the dry distillation of calcium benzoate, or by the action of benzene and aluminium chloride upon benzoyl chloride, or carbonyl chloride. This compound, although a true aromatic derivative, behaves exactly like an aliphatic ketone: on reduction, it yields *benzhydrol*, $C_6H_5\cdot CHOH\cdot C_6H_5$; *benzpinacone*,



$$\underset{OH}{(C_6H_5)_2C}-\!\!-\!\!-\underset{OH}{C(C_6H_5)_2}$$

is simultaneously formed (156).

Böeseken has explained the mechanism of Friedel and Crafts's synthesis (294, 2) of aromatic ketones. He has proved that the acid chloride first unites with the aluminium chloride:

$$C_6H_5COCl + AlCl_3 = C_6H_5COCl\cdot AlCl_3.$$

On addition of one molecule of benzene, one molecule of hydrochloric acid is evolved, with formation of a crystalline compound:

$$C_6H_5\cdot COCl\cdot AlCl_3 + C_6H_6 = C_6H_5\cdot CO\cdot C_6H_5\cdot AlCl_3 + HCl.$$

When this compound is treated with water, a quantitative yield of the ketone is obtained:

$$C_6H_5\cdot CO\cdot C_6H_5\cdot AlCl_3 + nH_2O = C_6H_5\cdot CO\cdot C_6H_5 + AlCl_3\cdot nH_2O.$$

The reaction therefore takes place in three stages.

Benzophenone exists in two modifications: one is unstable and melts at 27°; the other is stable and melts at 49°.

The relation of these substances to one another is one of *monotropy;* that is, at all temperatures up to its melting-point the metastable form changes to the stable form, but the process is not reversible. The explanation is that the transition-point of the two modifications is higher than the melting-point of the metastable isomeride.

For a substance with a transition-point (O), the vapour-pressure, p, in the neighbourhood of this point is represented by Fig. 79 ("Inorganic Chemistry," 70). AB is the vapour-pressure curve of the fused substance. Its direction must be such that on the right it lies lower than any other curve; that is, it must be nearest to the horizontal axis. Since rise of temperature ultimately occasions the fusion of all solid forms, above a certain temperature, definite for each substance, the liquid phase must be the most stable; in other words, it must have the lowest vapour-pressure. Of_1 is the melting-point of the metastable modification, which is higher than the transition-point: Of_2 is that of the stable modification.

AB can, however, be so situated that f_1 and f_2 are below *O* (Fig. 80). Here the melting-point is lower than the transition-point *O*, so that the latter cannot be attained. The metastable modification then remains in the metastable state up to its melting-point, the substance being *monotropic*. In the more usual case of *enantiotropy*, on rise of temperature the compound first attains the transition-point, then undergoes transformation, and finally melts.

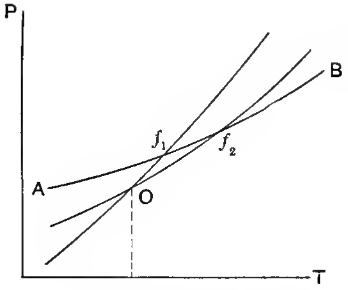


Fig. 79.—Enantiotropic Substance.

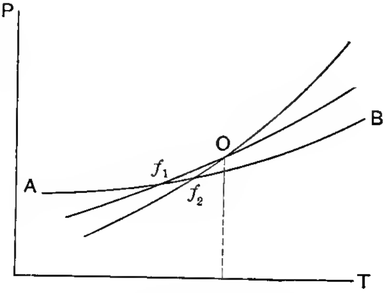
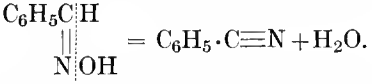


Fig. 80.—Monotropic Substance.

Oximes.

337. Some of the *oximes* of the aromatic aldehydes and ketones exhibit a peculiar kind of isomerism. Thus, there are two isomerides of benzaldoxime: *benz*anti*aldoxime* (α) melting at 35°; and *benz*syn*aldoxime* (β or *iso*), which melts at 128°, and on treatment with acetic anhydride readily loses water, forming benzonitrile:

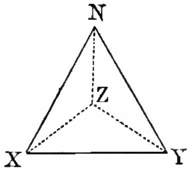


$$\begin{array}{l} C_6H_5C\,\vdots\,H \\ \quad\ \|\,\vdots \\ \quad N\,\vdots\,OH \end{array} = C_6H_5\cdot C\equiv N + H_2O.$$

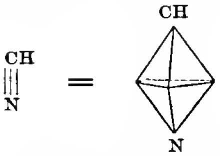
With acetic anhydride, the *anti*aldoxime yields an acetyl-derivative.

It has been proved that no isomerides of the ketoximes $\begin{smallmatrix} R \\ R' \end{smallmatrix}\!>C:NOH$ exist, when R and R′ are similar: when these groups are dissimilar, two isomerides are known. Benzophenoneoxime and its derivatives furnish examples. Despite many attempts to prepare an isomeride, benzophenoneoxime is known in only one modification. When, however, hydrogen in one phenyl-group is substituted, two isomeric oximes can be obtained. *Monochlorobenzophenone*, $C_6H_5\cdot CO\cdot C_6H_4Cl$, *monobromobenzophenone*, $C_6H_5\cdot CO\cdot C_6H_4Br$, *tolylphenylketone*, $CH_3 \cdot C_6H_4 \cdot CO \cdot C_6H_5$, and *anisylphenylketone*, $CH_3O \cdot C_6H_4 \cdot CO \cdot C_6H_5$, are examples of ketones which yield two isomeric oximes. Many other compounds of this type could be cited.

After several ineffectual attempts to explain such isomerism by the ordinary structural formulæ, the following stereochemical explanation of the observed facts has been adopted. It is assumed that the three affinities of the N-atom are directed towards the angles of a tetrahedron, the nitrogen atom itself being situated at the fourth angle:



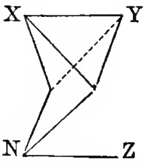
When the three nitrogen bonds are linked to carbon, as in the nitriles, the following spacial representation is obtained:



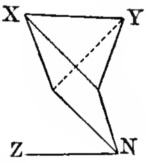
$$\begin{array}{c} CH \\ ||| \\ N \end{array}$$

Stereoisomerism is here impossible: experience has shown that none of the numerous nitriles known occurs in two forms due to isomerism in the CN-groups.

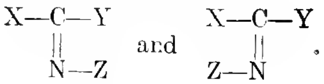
When, however, the nitrogen atom is linked to carbon by two bonds, two isomeric forms become possible:



and



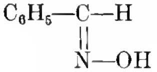
These can be more readily represented by



$$\begin{array}{l} X—C—Y \\ \quad \| \\ \quad N—Z \end{array} \quad \text{and} \quad \begin{array}{r} X—C—Y \\ \| \quad \\ Z—N \quad \end{array} .$$

It is apparent that different configurations for such compounds are only obtained when X and Y are different, since when they are similar the figures become identical. This agrees with the facts stated at the beginning of this section.

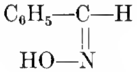
338. It can also be determined which configuration represents each isomeride. The two isomeric benzaldoximes have the formulæ



$$\begin{array}{rcl} C_6H_5- & C & -H \\ & \| & \\ & N & -OH \end{array}$$

Benzsynaldoxime
I.

and

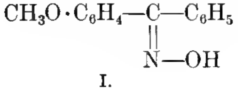


$$\begin{array}{rcl} C_6H_5- & C & -H \\ & \| & \\ HO- & N & \end{array}.$$

Benzantialdoxime
II.

In formula I., H and OH are nearer together than in formula **II.** This proximity explains the facility with which one molecule of water is eliminated from one aldoxime (*syn*), and not from the other (*anti*). On this account configuration I. is assigned to the *syn*aldoxime, and configuration II. to the *anti*aldoxime.

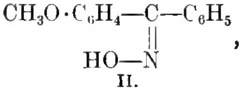
The configuration of the ketoximes can be determined by the Beckmann transformation (112), as is made clear in the following example. Two isomerides of *anisylphenylketoxime* are known,



$$\begin{array}{rcl} CH_3O\cdot C_6H_4- & C & -C_6H_5 \\ & \| & \\ & N & -OH \end{array}$$

I.

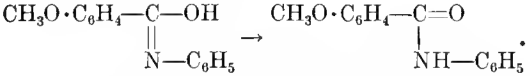
and



$$\begin{array}{rcl} CH_3O\cdot C_6H_4- & C & -C_6H_5 \\ & \| & \\ HO- & N & \end{array},$$

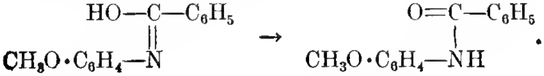
II.

the first melting at 137° and the second at 116°. By the Beckmann transformation, the oxime of higher melting-point yields the anilide of anisic acid; that of lower melting-point, the aniside of benzoïc acid. The former must therefore have configuration I., and the second configuration II., because in I. the groups OH and C_6H_5 are adjacent, and exchange places:



$$\begin{array}{rcl} CH_3O\cdot C_6H_4- & C & -OH \\ & \| & \\ & N & -C_6H_5 \end{array} \longrightarrow \begin{array}{rcl} CH_3O\cdot C_6H_4- & C & =O \\ & | & \\ & NH & -C_6H_5 \end{array}.$$

The anilide of anisic acid, $CH_3O\cdot C_6H_4\cdot COOH$, is thus produced. In II., anisyl ($CH_3O\cdot C_6H_4$—) and OH are adjacent, and exchange places, yielding the aniside of benzoïc acid:



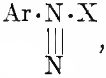
$$\begin{array}{rcl} HO- & C & -C_6H_5 \\ & \| & \\ CH_3O\cdot C_6H_4- & N & \end{array} \longrightarrow \begin{array}{rcl} O= & C & -C_6H_5 \\ & | & \\ CH_3O\cdot C_6H_4- & NH & \end{array}.$$

DIAZO-COMPOUNDS AND HYDRAZINES.

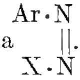
I. DIAZO-COMPOUNDS.

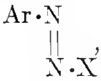
339. The diazo-compounds of the aromatic series, discovered by Griess in 1860, are not merely of theoretical importance, but play an important part in the manufacture of dyes. In the aliphatic series only amino-compounds of a special kind yield diazo-compounds (**233**), while their formation is a general reaction of the primary aromatic amines. *The property of undergoing diazotization is characteristic of aromatic amines.*

All diazo-compounds contain the group —N_2—. Hantzsch has classified them in two divisions.

I. Substances with the structural formula  $\begin{array}{c}\mathrm{Ar}\cdot\mathrm{N}\cdot\mathrm{X}\\ |||\\ \mathrm{N}\end{array}$, in which Ar represents phenyl, C_6H_5, and its homologues and derivatives. They are called *diazonium salts*, and are analogous to the ammonium salts.

II. Substances with the structural formula $\mathrm{Ar}\cdot\mathrm{N{=}N}\cdot\mathrm{X}$. These derivatives are called *diazo-compounds*, and resemble the azo-compounds. They are known in two stereoisomeric modifications.

1. Compounds with the stereochemical formula  $\begin{array}{c}\mathrm{Ar}\cdot\mathrm{N}\\ ||\\ \mathrm{X}\cdot\mathrm{N}\end{array}$. They are called syn*diazo-compounds*, are unstable, and can be isolated only in certain cases.

2. Compounds with the stereochemical formula  $\begin{array}{c}\mathrm{Ar}\cdot\mathrm{N}\\ ||\\ \mathrm{N}\cdot\mathrm{X}\end{array}$, or anti*diazo-compounds*, which are stable.

Intrinsically, the diazonium compounds are of slight importance, but the numerous transformations which they can undergo, with formation of a great number of derivatives, render them much more important than the diazo-compounds, and account for their great significance in the chemistry of the aromatic compounds.

Diazonium compounds are formed by the action of nitrous acid upon the salts of aromatic amines:

$$\underset{\text{Aniline nitrate}}{C_6H_5 \cdot NH_2 \cdot HNO_3} + HNO_2 = 2H_2O + \underset{\text{[Benzenediazonium nitrate}}{C_6H_5 \cdot N_2 \cdot NO_3}.$$

This is effected by adding a solution of sodium nitrite to a solution containing an equimolecular proportion of the amine-salt and an equivalent quantity of a free mineral acid, the reaction-mixture being cooled by the addition of ice, as the diazonium compounds decompose very readily. A solution of the benzenediazonium salt is thus obtained.

To isolate such a salt as *benzenediazonium chloride*, $C_6H_5 \cdot N_2 \cdot Cl$, in the solid state, a small quantity of concentrated hydrochloric acid is added to an alcoholic solution of aniline hydrochloride, and then amyl nitrite, whereupon the diazonium chloride crystallizes out. The dry diazonium salts are excessively explosive, and must, therefore, be handled with great care. In aqueous solution they are harmless, and as they yield derivatives without being isolated, they are seldom prepared in the solid state.

340. The constitution indicated for the diazonium salts is inferred from the following considerations.

The group N_2X of the diazonium compounds, in which X represents an acid-residue, is only linked to one carbon atom of the benzene-nucleus, for all their transformations produce substances containing a group likewise linked to only one carbon atom of the nucleus.

In many respects the group $C_6H_5 \cdot N_2$— behaves similarly to an alkali-metal, and still more to the ammonium radical. With strong mineral acids it forms colourless salts of neutral reaction, like KCl and NH_4Cl, while its salts with carbonic acid resemble the alkali-metal carbonates in having an alkaline reaction, due to hydrolytic dissociation. The conductivity of the diazonium salts of hydrochloric acid and other acids indicates that they are as strongly ionized as KCl and NH_4Cl. Similarly, diazonium chlorides yield complex platinum salts, such as $(C_6H_5N_2Cl)_2PtCl_4$, soluble with difficulty in water. Other analogous salts, such as $(C_6H_5N_2Cl)AuCl_3$, have also been obtained. Free *benzenediazonium hydroxide*, $C_6H_5\cdot N_2\cdot OH$, is only known in the form of an aqueous solution, which has a strongly alkaline reaction. It is obtained by treating the aqueous solution of the chloride with silver oxide, or by the addition of the equivalent quantity of baryta-water to the sulphate. Like caustic-potash solution, it is colourless, but through decomposition gradually deposits a flocculent, resin-like substance.

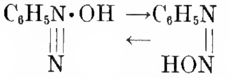
The existence of a quinquivalent N-atom in the diazonium salts, as in the ammonium salts, must therefore be assumed, the basic properties of the members of each class being due to its presence. Two formulæ are thus possible:

$$C_6H_5N{\equiv}N\cdot X \quad \text{or} \quad C_6H_5N\begin{smallmatrix}\diagup X\\ \diagdown\!\!\!\diagdown N\end{smallmatrix}.$$

For reasons given in **342**, the preference must be given to the second.

Benzenediazonium hydroxide is a strong base, but reacts with alkalis in a manner quite unknown among the strong mineral bases. When a diazonium salt is added to a strong solution of caustic potash, a potassium derivative, $C_6H_5\cdot N_2\cdot OK$, separates out. The reaction takes place not only in concentrated, but also in dilute, solutions. When a dilute solution of benzenediazonium hydroxide is treated with an equivalent quantity of caustic soda in dilute solution, the molecular conductivity of the mixture is considerably less than the sum of the two electric conductivities of the solutions separately. It follows that a portion of the ions $(C_6H_5N_2O)' + H^{\cdot}$ and $Na^{\cdot} + OH'$, which have been brought into contact, have changed to the non-ionized state—union of $H^{\cdot}$ and OH'; that is, a salt must have been formed.

Thus, the diazonium hydroxide, which is a strong base, appears to behave like an acid also. Since this is very improbable, HANTZSCH assumes that an equilibrium exists in the aqueous solution between the diazonium hydroxide and the *syn*diazohydroxide (**342**):



$$\begin{array}{ccc} C_6H_5N\cdot OH & \rightarrow & C_6H_5N \\ ||| & \leftarrow & || \\ N & & HON \end{array}$$

Diazonium hydroxide   *syn*Diazo-hydroxide

He supposes that the alkali-metal compounds are derived from the latter substance.

Reactions of the Diazonium Compounds.

341. Many of the reactions of the diazonium compounds are characterized by the elimination from the molecule of the group —N_2— as free nitrogen, and its replacement by a substituent linked by a single bond to the benzene-nucleus. Extended research has revealed the conditions best suited for obtaining nearly quantitative results in most of these reactions.

1. *Replacement of the N_2-group by hydroxyl.*—This reaction is effected by allowing the aqueous solution of the diazonium salt to stand, or by warming it:

$$C_6H_5\cdot N_2\cdot Cl + HOH = C_6H_5\cdot OH + N_2 + HCl.$$

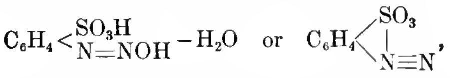
2. *Replacement by an alkoxyl-group,* —$O\cdot C_nH_{2n+1}$.—This replacement is carried out by boiling a diazonium salt with alcohol:

$$C_6H_5\cdot N_2\cdot \boxed{HSO_4+H}O\cdot C_2H_5 = C_6H_5O\cdot C_2H_5 + N_2 + H_2SO_4.$$

3. *Replacement of the diazonium-group by hydrogen.*—Under certain conditions the diazonium salts do not yield alkoxyl-compounds with alcohols, but produce the corresponding hydrogen compound, the alcohol being converted into aldehyde:

$$\underset{\text{p-Nitrobenzenediazonium chloride}}{NO_2\cdot C_6H_4\cdot N_2\cdot Cl} + C_2H_5OH = \underset{\text{Nitrobenzene}}{NO_2\cdot C_6H_5} + \underset{\text{Acetaldehyde}}{C_2H_4O} + N_2 + HCl.$$

By this treatment, p-*diazobenzenesulphonic acid,*



$$C_6H_4<{SO_3H \atop N{=}NOH} - H_2O \quad \text{or} \quad C_6H_4\Big\langle {SO_3 \atop {| \atop N{\equiv}N}},$$

when treated with methyl alcohol under diminished pressure, yields only benzenesulphonic acid, the diazonium-group being therefore only replaced by hydrogen. Under a pressure of thirty atmospheres, however, only *anisolesulphonic acid,* $C_6H_4<{SO_3H \atop OCH_3}$, is formed, N_2 being replaced by the methoxyl-group, —OCH_3.

4. *Replacement of the diazonium-group by halogens.*—This reaction is effected by treating a solution of diazonium chloride either

with cuprous chloride dissolved in concentrated hydrochloric acid (Sandmeyer), or with finely-divided copper (Gattermann):

$$C_6H_5 \cdot N_2 \cdot Cl = C_6H_5 \cdot Cl + N_2.$$

Cuprous chloride and finely-divided copper have a catalytic action: it is probable that a copper compound is formed as an intermediate product, and afterwards decomposed.

Replacement by bromine is carried out similarly: thus, in the preparation of bromobenzene, a solution of potassium bromide is added to an aqueous solution of benzenediazonium sulphate containing free sulphuric acid; on addition of copper-dust to this mixture, nitrogen is evolved, and bromobenzene formed.

Replacement by iodine takes place readily when a warm solution of potassium iodide is added to a diazonium-sulphate solution: it is unnecessary to employ copper or cuprous chloride.

5. *Replacement of the diazonium-group by the* CN-*group.*—This replacement, too, readily takes place in presence of copper compounds. The solution of the diazonium salt is added to one of potassium cuprous cyanide:

$$C_6H_5 \cdot N_2 \cdot Cl + KCN = C_6H_5 \cdot CN + N_2 + KCl.$$

This reaction is of great importance for the synthesis of aromatic acids, which can be obtained by hydrolyzing the resulting nitriles.

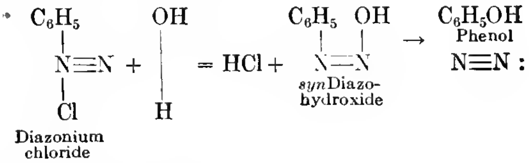
6. *Other reactions.*—When diazonium salts react with sulphuretted hydrogen, compounds containing sulphur linked to the benzene-nucleus are produced. By this treatment, benzenediazonium chloride yields phenyl sulphide, $(C_6H_5)_2S$, two molecules of the chloride reacting with one of sulphuretted hydrogen.

The N_2-group can also be replaced by aromatic hydrocarbon-residues. Thus, *diphenyl*, $C_6H_5 \cdot C_6H_5$, is obtained by treating dry benzenediazonium chloride with benzene in presence of a small quantity of aluminium chloride:

$$C_6H_5 \cdot N_2 \cdot Cl + H \cdot C_6H_5 = C_6H_5 \cdot C_6H_5 + N_2 + HCl.$$

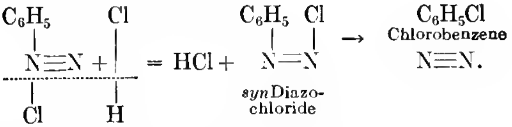
These reactions illustrate the importance of the diazonium salts as intermediate products in the preparation of numerous substances. Since they are derived from the amines, which are prepared by the reduction of nitro-compounds, it is evident that the nitration of aromatic derivatives is a reaction of great importance, for the nitro-group can be replaced at will by almost all other elements or groups by means of the amino-compounds and diazonium compounds.

342. Hantzsch has explained the reactions of the diazonium compounds by assuming that they themselves do not enter into reaction, but are first converted into *syn*diazo-compounds, which then decompose with evolution of nitrogen. The formation of phenol must be represented thus:



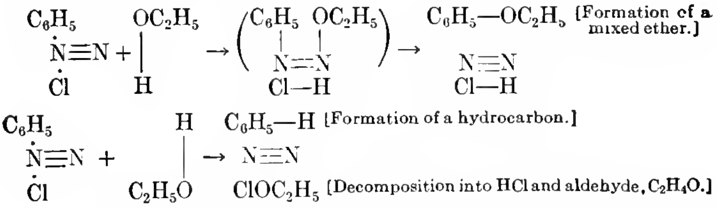
$$\begin{array}{c}C_6H_5\\|\\N\equiv N\\|\\Cl\\\text{Diazonium}\\\text{chloride}\end{array}+\begin{array}{c}OH\\|\\|\\|\\H\end{array}=HCl+\begin{array}{c}C_6H_5\quad OH\\|\qquad|\\N=N\\\textit{syn}\text{Diazo-}\\\text{hydroxide}\end{array}\rightarrow\begin{array}{c}C_6H_5OH\\\text{Phenol}\\N\equiv N:\end{array}$$

and that of chlorobenzene thus:



$$\begin{array}{c}C_6H_5\qquad Cl\\|\qquad\quad|\\N\equiv N+|\\\hline|\qquad\quad|\\Cl\qquad H\end{array}=HCl+\begin{array}{c}C_6H_5\ Cl\\|\quad|\\N=N\\\textit{syn}\text{Diazo-}\\\text{chloride}\end{array}\rightarrow\begin{array}{c}C_6H_5Cl\\\text{Chlorobenzene}\\N\equiv N.\end{array}$$

The reactions between diazonium salts and alcohols are explained as follows:



$$\begin{array}{c}C_6H_5\\\dot{N}\equiv N\\\dot{Cl}\end{array}+\begin{array}{c}OC_2H_5\\|\\H\end{array}\rightarrow\left(\begin{array}{c}C_6H_5\ OC_2H_5\\|\qquad|\\N=N\\Cl-H\end{array}\right)\rightarrow\begin{array}{c}C_6H_5-OC_2H_5\\N\equiv N\\Cl-H\end{array}\text{[Formation of a mixed ether.]}$$

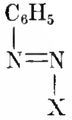
$$\begin{array}{c}C_6H_5\\\dot{N}\equiv N\\\dot{Cl}\end{array}+\begin{array}{c}H\\|\\C_2H_5O\end{array}\rightarrow\begin{array}{l}C_6H_5-H\ \text{[Formation of a hydrocarbon.]}\\N\equiv N\\ClOC_2H_5\ \text{[Decomposition into HCl and aldehyde, }C_2H_4O\text{.]}\end{array}$$

As these transformations of diazonium salts cannot be represented by the aid of the other possible structural formula, $C_6H_5\cdot N\equiv N\cdot X$, it is evident that it must be rejected (340).

Most of the *syn*diazo-compounds are very unstable. They change readily into *anti*diazo-compounds, in which it is assumed that the phenyl-group and acid-residue are not contiguous, and therefore can no longer unite:

$$\begin{array}{c}C_6H_5\ X\\|\qquad|\\N=N\end{array}$$

*syn*Diazo-compound; C_6H_5 and X can unite

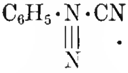


$$\begin{array}{c}C_6H_5\\|\\N=N\\|\\X\end{array}$$

*anti*Diazo-compound; C_6H_5 and X cannot unite

In certain cases, such as that of the diazocyanides, HANTZSCH has been able to isolate these intermediate products, and thus afford a proof of these views. For example, when cyanides are added to diazotized p-*chloroaniline*, $Cl\cdot C_6H_4\cdot NH_2$, p-*chlorobenzonitrile*, $Cl\cdot C_6H_4\cdot CN$, is not immediately formed: it is possible to isolate a yellow intermediate product, $Cl\cdot C_6H_4\cdot N_2\cdot CN$, which yields *p*-chlorobenzonitrile after addition of copper-dust, the action being accompanied by an energetic evolution of nitrogen. This yellow intermediate p-*chlorobenzene*syn*diazocyanide* is, however, very unstable, and speedily changes to an isomeride (the *anti*-compound) which does not react with copper-dust. Stereochemical theory thus affords a satisfactory explanation of the observed phenomena.

It might be suggested that the unstable primary product is diazonium cyanide,

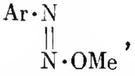


$$\begin{array}{l}C_6H_5\cdot N\cdot CN\\ |||\\ N\end{array}\ .$$

It is evident that it is not, for such a cyanide must have properties analogous to those of potassium cyanide; it must be colourless, like the other diazonium salts, and it must have an alkaline reaction in aqueous solution, and conduct electricity, whereas the unstable primary product possesses none of these properties.

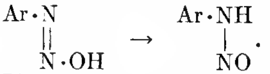
Moreover, an anisole derivative, $CH_3O\cdot C_6H_4N_2\cdot CN$, was discovered by HANTZSCH, which must be looked upon as a diazonium cyanide, since its aqueous solution exhibits all these properties.

The anti*diazoxides*, or anti*diazotates*,



$$\begin{array}{l}Ar\cdot N\\ \|\\ N\cdot OMe\end{array},$$

are readily converted by addition of acids into nitrosoamines. Free anti*diazohydroxides*, or anti*diazohydrates*, react thus:



$$\begin{array}{l}Ar\cdot N\\ \|\\ N\cdot OH\end{array} \longrightarrow \begin{array}{l}Ar\cdot NH\\ |\\ NO\end{array}.$$

*anti*Diazohydroxide Nitrosoamine

The relation of these two classes of compounds to each other is that of acids to *pseudo*-acids. The *anti*diazohydroxides exhibit the reactions characteristic of the hydroxyl-group, and most of them are—especially in solution—very unstable. They are rapidly converted into the corresponding *pseudo*-acids, or nitrosoamines, from which alkalis at once regenerate the corresponding *anti*diazoxides.

In accordance with the foregoing formula, the nitrosoamines, unlike the *anti*diazohydroxides, are indifferent towards reagents for the hydroxyl-group. Their *pseudo*-acidic character is indicated by the facts that they are non-electrolytes of neutral reaction, and do not form salts with ammonia.

343. The importance of the diazonium compounds is not confined to reactions in which the nitrogen atoms are eliminated, since important derivatives in which they are retained are known.

1. *Diazoamino-compounds* are obtained by the action of primary and secondary amines upon diazonium salts:

$$C_6H_5\cdot N_2\cdot \boxed{Cl+H}NHC_6H_5 = \underset{\text{Diazoaminobenzene}}{C_6H_5\cdot N_2\cdot NHC_6H_5}+HCl.$$

They are also produced when nitrous acid reacts with free aniline, instead of with an aniline salt. It may be supposed that in this reaction benzenediazonium hydroxide, or benzenediazohydroxide is first formed, and is at once attacked by a molecule of the aniline still present:

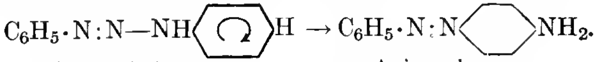
$$\text{I. } C_6H_5\cdot NH_2+HNO_2 = C_6H_5\cdot N_2\cdot OH+H_2O.$$

$$\text{II. } \underset{\text{Benzenediazohydroxide}}{C_6H_5\cdot N_2\cdot \boxed{OH+H}}NHC_6H_5 = C_6H_5\cdot N:N\cdot NHC_6H_5+H_2O.$$

The diazoamino-compounds are crystalline, and have a yellow colour. They do not unite with acids. In acid solution, they are converted by treatment with nitrous acid into diazonium salts:

$$C_6H_5\cdot N:N\cdot NHC_6H_5+HNO_2+2HCl = 2C_6H_5\cdot N_2\cdot Cl+2H_2O.$$

The most characteristic property of the diazoamino-compounds is the readiness with which they can be transformed into isomerides, the *aminoazo-compounds:*



Diazoaminobenzene

Aminoazobenzene

This is effected by adding aniline hydrochloride to a solution of diazoaminobenzene in aniline, and warming the mixture on the water-bath.

The amino-group in *aminoazobenzene* is in the *para*-position to the azo-group. When the *para*-position is already occupied, the amino-group takes up the *ortho*-position. Aminoazobenzene and many of its derivatives are dyes (361).

The equation indicates that the transformation of diazoaminobenzene into aminoazobenzene is a unimolecular reaction ("Inorganic Chemistry," 50). GOLDSCHMIDT proved by experiment that this view is correct. He dissolved diazoaminobenzene in aniline, and determined the quantity of diazoaminobenzene still present after the lapse of known periods of time.

The aniline hydrochloride added in this reaction has merely a catalytic, accelerating effect upon the reaction, as is proved, *inter alia*, by the uniform rise in the velocity-constant with increase in the amount of aniline hydrochloride.

2. Diazonium salts unite with tertiary amines at the *para*-position:

$$C_6H_5 \cdot N_2 \cdot \boxed{Cl + H}\underset{\text{Dimethylaniline}}{C_6H_4 \cdot N(CH_3)_2} = \underset{\text{Dimethylaminoazobenzene}}{C_6H_5 \cdot N:N \cdot C_6H_4 \cdot N(CH_3)_2} + HCl.$$

3. They react similarly with phenols, forming *hydroxyazo-compounds*. This combination takes place in presence of alkalis:

$$C_6H_5 \cdot N_2 \cdot \boxed{Cl + H}\underset{\text{Phenol}}{C_6H_4OH} = \underset{\text{Hydroxyazobenzene}}{C_6H_5 \cdot N:N \cdot C_6H_4OH} + HCl.$$

Important dyes are also derived from *hydroxyazobenzene* (363).

II. HYDRAZINES.

344. The typical derivative of hydrazine is *phenylhydrazine*, $C_6H_5 \cdot NH \cdot NH_2$, referred to several times in the aliphatic series in connection with its action on aldehydes, ketones, and sugars (112, 205, and 209). It is formed by the reduction of the diazonium salts; for example, from benzenediazonium chloride by the action of the calculated quantity of stannous chloride dissolved in hydrochloric acid:

$$C_6H_5 \cdot N_2 \cdot Cl + 4H = C_6H_5 \cdot NH{-}NH_2 \cdot HCl.$$

It can also be obtained by transforming the diazonium salt into a diazosulphonate by means of an alkali-metal sulphite, reducing the diazosulphonate with zinc-dust and acetic acid, and eliminating the sulpho-group by boiling with hydrochloric acid:

$$\text{I.}\quad C_6H_5 \cdot N_2 \cdot Cl + Na_2SO_3 = \underset{\text{Sodium diazobenzenesulphonate}}{C_6H_5 \cdot N:N \cdot SO_3Na} + NaCl.$$

$$\text{II.}\quad C_6H_5 \cdot N:N \cdot SO_3Na + 2H = \underset{\text{Sodium phenylhydrazinesulphonate}}{C_6H_5 \cdot NH \cdot NH \cdot SO_3Na}.$$

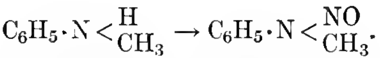
$$\text{III.}\quad C_6H_5 \cdot NH \cdot NH \cdot SO_3Na + H_2O = \underset{\text{Phenylhydrazine}}{C_6H_5 \cdot NH \cdot NH_2} + NaHSO_4.$$

In practice, this apparently roundabout way is simple, since the intermediate products need not be isolated. It is sufficient to mix solutions of the diazonium salt and of the sulphite, add the acetic acid and zinc-dust, and filter off the excess of zinc. The filtrate is then boiled with fuming hydrochloric acid, whereupon the hydrochloride, $C_6H_5 \cdot NH \cdot NH_2 \cdot HCl$, separates out, being soluble with difficulty in water, and almost insoluble in hydrochloric acid.

Phenylhydrazine is a colourless, oily liquid, turning brown in the air. Its melting-point is 19·6°, and its boiling-point 241°: when boiled under ordinary pressure, it undergoes slight decomposition. It is only slightly soluble in water.

Phenylhydrazine is decomposed by energetic reduction into aniline and ammonia. It is very sensitive towards oxidizing agents, its sulphate being oxidized to the diazonium salt by mercuric oxide. Oxidation usually goes further, however, the nitrogen being eliminated from the molecule. Thus, an alkaline copper solution converts it into water, nitrogen, and benzene. Phenylhydrazine has a wholly basic character: it yields well-defined crystalline salts.

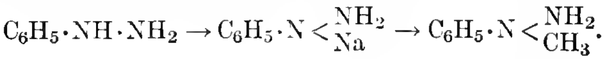
Phenylhydrazine is proved thus to have the constitutional formula $C_6H_5 \cdot NH \cdot NH_2$. A secondary amine is converted by nitrous acid into the corresponding nitrosoamine:



$$C_6H_5 \cdot N < \begin{matrix} H \\ CH_3 \end{matrix} \rightarrow C_6H_5 \cdot N < \begin{matrix} NO \\ CH_3 \end{matrix}.$$

Monomethylaniline Nitrosomethylaniline

On careful reduction, this substance yields *methylphenylhydrazine*, $C_6H_5 \cdot N < \begin{matrix} NH_2 \\ CH_3 \end{matrix}$, which can also be obtained from phenylhydrazine by the action of sodium, one hydrogen atom being replaced by the metal. On treatment of this sodium compound with methyl iodide, the same methylphenylhydrazine is formed:



$$C_6H_5 \cdot NH \cdot NH_2 \rightarrow C_6H_5 \cdot N < \begin{matrix} NH_2 \\ Na \end{matrix} \rightarrow C_6H_5 \cdot N < \begin{matrix} NH_2 \\ CH_3 \end{matrix}.$$

COMPOUNDS CONTAINING AN UNSATURATED SIDE-CHAIN.

Hydrocarbons.

345. *Styrole*, $C_6H_5\cdot CH:CH_2$, derives its name from its occurrence in storax. It can be obtained from cinnamic acid, $C_6H_5\cdot CH:CH\cdot COOH$, by heating it, whereupon carbon dioxide is eliminated. It is a liquid of agreeable odour, and boils at 146°. On treatment with nitric acid, it yields *nitrostyrole*, $C_6H_5\cdot CH:CH\cdot NO_2$, with the nitro-group in the side-chain. The constitution of this compound follows from its formation by the condensation of benzaldehyde with nitromethane, under the catalytic influence of alcoholic potash:

$$C_6H_5\cdot\overset{H}{C}\boxed{O+H_2}CH\cdot NO_2 = C_6H_5\cdot CH:CH\cdot NO_2+H_2O.$$

Phenylacetylene, $C_6H_5\cdot C\equiv CH$, can be obtained by treating acetophenone with phosphorus pentachloride, and acting on the resulting compound, $C_6H_5\cdot CCl_2\cdot CH_3$, with caustic potash; or from phenylpropiolic acid, $C_6H_5\cdot C\vdots C\cdot COOH$, by heating its cupric salt with water. In many respects it resembles acetylene; for example, it yields metallic derivatives. On solution in concentrated sulphuric acid, it takes up one molecule of water, forming acetophenone.

Alcohols and Aldehydes.

346. *Cinnamyl alcohol*, $C_6H_5\cdot CH:CH\cdot CH_2OH$, is the only representative of the unsaturated alcohols which need be mentioned. It is a crystalline substance with an odour of hyacinths, and is present as an ester in storax. Careful oxidation converts it into cinnamic acid (**348**), and more vigorous oxidation into benzoïc acid.

347. *Cinnamaldehyde*, $C_6H_5\cdot CH:CH\cdot C\overset{H}{\underset{O}{}}$, is the chief constituent of oil of cinnamon, from which it can be obtained by means of its sulphite compound. It is an oil of agreeable odour, and boils at 246° It is resinified by strong acids, and with ammonia yields *hydrocinnamide*, $N_2(C_6H_5C_3H_3)_3$, analogous to hydrobenzamide (**335**).

Acids.

348. *Cinnamic acid*, $C_6H_5\cdot CH:CH\cdot COOH$, is the most important unsaturated acid. It is present in some balsams, and in storax. It is manufactured by a synthetic method discovered by

Sir William Perkin. Benzaldehyde is heated with acetic anhydride, in presence of sodium acetate as a catalyst:

$$\underset{\text{Benzaldehyde}}{C_6H_5\cdot C\overset{H}{\underset{O}{}}}+\underset{\text{Acetic anhydride}}{H_2CH\cdot CO\cdot O\cdot CO\cdot CH_3}=C_6H_5\cdot CH:CH\cdot CO\cdot O\cdot CO\cdot CH_3;$$

$$+H_2O = \underset{\text{Cinnamic acid}}{C_6H_5\cdot CH:CH\cdot COOH}+\underset{\text{Acetic acid}}{HO\cdot CO\cdot CH_3}.$$

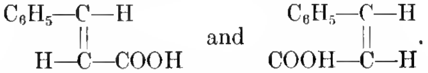
Perkin's synthesis can be carried out with substituted benzaldehydes on the one hand, and with homologues of acetic acid or with dibasic acids on the other, so that it is possible to obtain a great number of unsaturated aromatic acids by its aid.

Cinnamic acid can also be got by the action of benzal chloride (351), $C_6H_5\cdot CHCl_2$, upon sodium acetate. It can further be synthesized by the condensation of malonic acid with benzaldehyde, which takes place readily under the catalytic influence of ammonia, one molecule of carbon dioxide being eliminated:

$$\underset{\text{Malonic acid}}{(HOOC)_2C}\boxed{H_2+O}\genfrac{}{}{0pt}{}{C\cdot C_6H_5}{H} = C_6H_5\cdot CH:CH\cdot COOH+CO_2+H_2O.$$

Cinnamic acid is a crystalline substance, melts at 134°, and dissolves with difficulty in cold water. In all respects it possesses the character of a substance with a double bond, and therefore forms addition-products and reduces von Baeyer's reagent (123).

Its constitution indicates that two stereoisomerides are possible:



$$\begin{matrix}C_6H_5-C-H\\ \|\\ H-C-COOH\end{matrix}\quad\text{and}\quad\begin{matrix}C_6H_5-C-H\\ \|\\ COOH-C-H\end{matrix}.$$

Four isomerides, however, are known: ordinary cinnamic acid; *allocinnamic acid*, melting at 68°; and two *isocinnamic acids*, melting at 58° and 42° respectively. Bülman has proved that the last three acids are modifications of a single form, and therefore afford an example of trimorphism. On inoculating the liquid, obtained by fusion of any of them, with one of the forms, that form crystallizes out. *Allo*cinnamic acid and the *iso*cinnamic acids can be prepared by partial reduction of phenylpropiolic acid, $C_6H_5\cdot C{\equiv}C\cdot COOH$ (345); and must, therefore, have the *cis*-configuration (I.), as is evident from a model. It follows that ordinary cinnamic acid has the *trans*-configuration (II.):

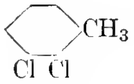
$$\text{I.}\ \begin{matrix}H\cdot C\cdot C_6H_5\\ \|\\ H\cdot C\cdot COOH\end{matrix};\qquad \text{II.}\ \begin{matrix}C_6H_5\cdot C\cdot H\\ \|\\ H\cdot C\cdot COOH\end{matrix}.$$

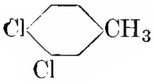
Cis *Trans*

It can be converted into the *cis*-acids by the action of the ultraviolet rays of a "uviol" lamp.

POLYSUBSTITUTED DERIVATIVES CONTAINING SIMILAR SUBSTITUENTS.

349. The number of polysubstituted derivatives of benzene and its homologues is very great. The hydrogen atoms of these hydrocarbons can be replaced not only by two or more similar groups, but also by two or more different groups. For each disubstitution-product and for each trisubstitution-product of benzene three isomerides are possible when the substituents are similar. In the homologues of benzene, substitution can take place wholly or partly in the side-chain: thus, the following isomerides are theoretically possible for a compound $C_7H_6Cl_2$:


(1)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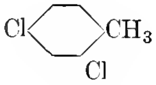
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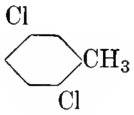
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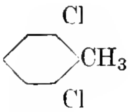
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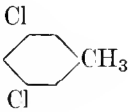
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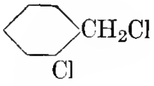
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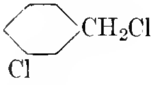
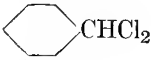

(8)


(9)


(10)

A large proportion of the numerous theoretically possible compounds is known. Only a few typical examples can be considered.

It would be impossible to describe the determination of position

—*orientation*—of the substituents in each of these compounds: a summary of orientation-methods is given in 398 to 403.

I. POLYSULPHONIC ACIDS.

350. When benzene and its homologues are treated with fuming sulphuric acid, disulphonic acids and trisulphonic acids, very similar in properties to the monosulphonic acids, are formed. Thus, benzene yields m-*benzenedisulphonic acid*, which is partially converted into p-*benzenedisulphonic acid* on prolonged heating; but heating with concentrated sulphuric acid partially reconverts *p*-benzenedisulphonic acid into the *meta*-form.

II. POLYHALOGEN DERIVATIVES.

351. The aromatic *polyhalogen derivatives* can be obtained by the direct action of chlorine or bromine upon the aromatic hydrocarbons. If one halogen atom is already present, substitution takes place principally in the *p*-position, a small quantity of the *o*-compound being also formed. m-*Dichlorobenzene* or m-*dibromobenzene* is obtained from *m*-dinitrobenzene (359) by reducing to diamine and subsequently diazotizing. It has been found possible by prolonged halogenation to replace the six hydrogen atoms of benzene by halogen. JULINS's *chlorocarbon*, C_6Cl_5, is thus obtained in the form of colourless needles melting at 229°. It has not been possible to replace all the hydrogen atoms in toluene by chlorine: it has only been converted into *tetrachlorobenzotrichloride*, $C_6HCl_4 \cdot CCl_3$, or into *pentachlorobenzal chloride*, $C_6Cl_5 \cdot CHCl_2$. On further chlorination, the molecule is decomposed. Examples of this phenomenon are also found in the aliphatic series.

The same methods can be employed in the preparation of the polyhalogen derivatives of the homologues of benzene as have been described for the monohalogen derivatives (299). If it is desired to substitute only its methylhydrogen atoms, toluene is treated with chlorine or bromine at the boiling-point: there are obtained in succession *benzyl chloride*, $C_6H_5 \cdot CH_2Cl$, *benzal chloride*, $C_6H_5 \cdot CHCl_2$, and *benzotrichloride*, $C_6H_5 \cdot CCl_3$. When the object is to substitute hydrogen only in the ring, chlorine is allowed to react at ordinary temperatures in presence of a trace of iodine. To prepare a compound such as $C_6H_4Cl \cdot CH_2Cl$, both methods must be employed in succession.

Benzal chloride, $C_6H_5 \cdot CHCl_2$ (B.P. 206°), and benzotrichloride, $C_6H_5 \cdot CCl_3$ (B.P. 213°), are of technical importance. Benzaldehyde (335) is obtained from the former, and benzoïc acid (331) from the latter.

Benzene and some of its homologues also yield addition-products with chlorine and bromine. From benzene is obtained *benzene hexachloride*, $C_6H_6Cl_6$, and *benzene hexabromide*, $C_6H_6Br_6$. Both are got by treating benzene with excess of the halogen in presence of sunlight. The chlorine derivative exists in two isomeric forms.

III. POLYHYDRIC PHENOLS.

352. Phenol is much more readily attacked by oxidizing agents than benzene (303). The *polyhydric phenols* possess this property to an even greater extent, many of them behaving as powerful reducing agents when dissolved in alkalis.

Dihydric Phenols.

353. The *o*-compound, $C_6H_4<\begin{array}{l}OH\ 1\\ OH\ 2\end{array}$, *catechol* ("pyrocatechol" or "pyrocatechin"), is a constituent of many resins, and can be prepared by fusing *o*-phenolsulphonic acid with caustic potash.

Catechol is crystalline and readily soluble in water, alcohol, and ether. It melts at 104°. Its alkaline solution is first turned green by atmospheric oxidation, and then black. Its aqueous solution precipitates metallic silver from silver-nitrate solution at ordinary temperatures, and gives a green coloration with ferric chloride. The monomethyl ether, $C_6H_4<\begin{array}{l}OCH_3\ 1\\ OH\ \ \ \ \ \ 2\end{array}$, is called *guaiacol:* it is present in the tar obtained by the dry distillation of beechwood. When heated with hydriodic acid, guaiacol yields catechol and methyl iodide.

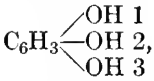
Resorcinol ("resorcin"), or *m*-dihydroxybenzene, $C_6H_4<\begin{array}{l}OH\ 1\\ OH\ 3\end{array}$, can be obtained by fusing *m*-phenylenedisulphonic acid, $C_6H_4<\begin{array}{l}SO_3H\ 1\\ SO_3H\ 3\end{array}$, with caustic potash, the method for its manufacture. It yields a deep-violet coloration with ferric chloride:

bromine-water converts it into *tribromoresorcinol.* It is a colourless, crystalline substance melting at 118°, and is readily soluble in water, alcohol, and ether. It quickly turns brown, owing to the action of the air.

Quinol ("hydroquinone"), or *p*-dihydroxybenzene, melts at 169°. Its chief characteristic is the loss on oxidation of two hydrogen atoms with formation of *quinone,* $C_6H_4O_2$ (356), which is readily reconverted into quinol by reduction. The reducing effect of quinol is employed in photography for the development of negatives. With ammonia it gives a red-brown coloration, due to the formation of complex derivatives. Like its isomerides, it is readily soluble in water.

Trihydric Phenols.

354. ***Pyrogallol*** ("pyrogallic acid"),

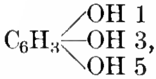


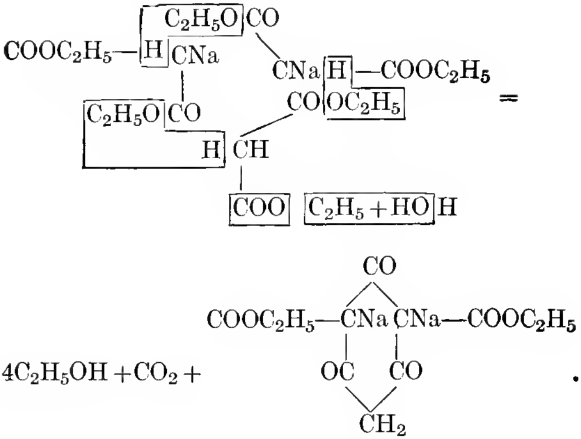
$$C_6H_3\left\langle\begin{array}{l}OH\ 1\\ OH\ 2,\\ OH\ 3\end{array}\right.$$

is obtained by heating *gallic acid* (388), CO_2 being split off:

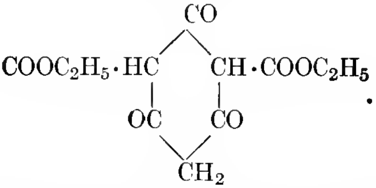
$$\underset{\text{Gallic acid}}{C_6H_2(OH)_3\cdot COOH} = \underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + CO_2.$$

Pyrogallol forms crystals melting at 132°, and is readily soluble in water. It is a strong reducing agent in alkaline solution: for example, it rapidly absorbs the oxygen of the atmosphere, with formation of a brown coloration. For this reason it is employed in gas-analysis to remove oxygen from mixtures. It also finds application as a developer in photography.

Phloroglucinol (symmetrical trihydroxybenzene),  $C_6H_3\left\langle\begin{array}{l}OH\ 1\\ OH\ 3,\\ OH\ 5\end{array}\right.$ is formed by fusing various resins with caustic potash. It is crystalline, and gives a deep-violet coloration with ferric chloride. A remarkable synthesis of phloroglucinol has been discovered by VON BAEYER. When diethyl sodiomalonate (166) is heated with diethyl malonate, three molecules condense, with elimination of four molecules of alcohol and one molecule of carbon dioxide:

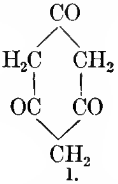


MOORE has shown that during the condensation one ethyl-carboxyl-group is eliminated, and that acidification of the condensation-product replaces the sodium atoms by hydrogen, with formation of *diethyl phloroglucinoldicarboxylate*,

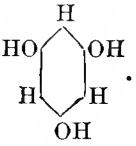


When this substance is fused with caustic potash, the ethyl-carboxyl-groups (—$COOC_2H_5$) are replaced by hydrogen, phloroglucinol resulting.

Phloroglucinol should therefore have constitution **I.**



I.



II.

In other words, it is a hexamethylene in which three of the methylene-groups, $=CH_2$, have been replaced by carbonyl, $=CO$: it must, therefore, be called *triketohexamethylene.* It has been proved that phloroglucinol does behave as though it had this constitution: thus, with three molecules of hydroxylamine it yields a trioxime. On the other hand, phloroglucinol has the character of a phenol: for example, it yields a triacetate with acetyl chloride. It exists, therefore, in two tautomeric forms—as a hexamethylene derivative, I., and as trihydroxybenzene, II.

This is a remarkable example of the alteration of the positions of the atoms (the hydrogen of the OH-groups) in the molecule, resulting in the conversion of a benzene derivative into a derivative of hexamethylene.

This view explains the interaction of phloroglucinol, and other polyhydric phenols, and a mixture of caustic potash and an alkyl iodide to form derivatives with alkyl-groups attached to carbon and not to oxygen; for the hydrogen in the methylene-groups of the tautomeric form must be replaceable by metals (200).

Higher Phenols.

355. The chief of the *higher phenols* is *hexahydroxybenzene*, $C_6(OH)_6$. Its potassium derivative, *potassium carbonyl*, $C_6(OK)_6$, is formed in the preparation of potassium, and acquires an explosive character on exposure to the air ("Inorganic Chemistry," 227). It can be obtained by heating potassium in a current of carbon monoxide, a direct synthesis of a derivative of benzene. Distillation with zinc-dust converts hexahydroxybenzene into benzene. It is a white, crystalline substance, and undergoes oxidation very readily.

IV. QUINONES.

356. The *quinones* are substances derived by the elimination of two hydroxyl-hydrogen atoms from aromatic dihydroxy-derivatives:

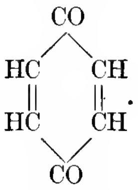
$$\underset{\text{Dihydroxybenzene}}{C_6H_4(OH)_2 - 2H} = \underset{\text{Quinone}}{C_6H_4O_2}.$$

The simplest quinone is *benzoquinone*, $C_6H_4O_2$: it is also called *quinone*. It is obtained by the oxidation of many *p*-derivatives of benzene, such as *p*-aminophenol $C_6H_4{<}\begin{matrix}NH_2 & 1\\ OH & 4\end{matrix}$, sulphanilic acid, $C_6H_4{<}\begin{matrix}NH_2 & 1\\ SO_3H & 4\end{matrix}$, and *p*-phenolsulphonic acid, $C_6H_4{<}\begin{matrix}OH & 1\\ SO_3H & 4\end{matrix}$, and also by the oxidation of aniline with chromic acid—the ordinary method of preparation. It is also formed in the oxidation of quinol

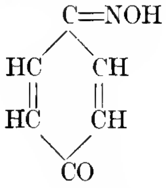
(**353**), though the latter is usually prepared by the reduction of quinone.

> *o*-Dihydroxybenzene or catechol can also be converted by the action of silver oxide into an unstable quinone. *m*-Dihydroxybenzene or resorcinol does not yield a quinone.

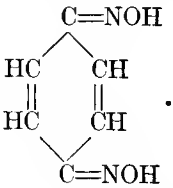
The quinones are yellow, and have a peculiar, pungent odour. They volatilize with steam with partial decomposition, and have oxidizing properties. The constitution of benzoquinone is best expressed by



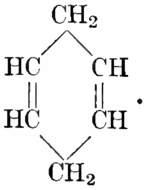
Such a formula requires that benzoquinone should be a diketone, and contain two double bonds: its properties show that it fulfils both conditions. Its ketonic character is inferred from its yielding with hydroxylamine first a *quinone mono-oxime* (**381**), and then a *quinone-dioxime:*



and



The presence of double linkings is proved by its power of forming addition-products: benzoquinone in chloroform solution can take up four atoms of bromine. According to this constitution, benzoquinone is not a true benzene derivative, but the *p*-diketone of a dihydrobenzene:



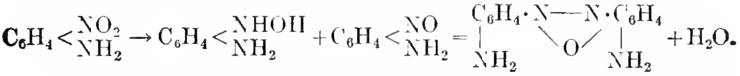
357. Some apparent exceptions to HABER'S scheme (**327**) for the electro-reduction of nitro-compounds are explained by assuming that quinone derivatives are formed as intermediate products. These exceptions have been observed in the reduction of higher-substituted nitrobenzene derivatives in alcoholic-alkaline solution. According to the scheme, azo-derivatives should be the chief products under these conditions, whereas in some instances amines are principally produced. Thus, the main product obtained from *p*-nitroaniline is *p*-phenylenediamine, while under the same conditions *m*-nitroaniline in a normal manner yields *m*-diaminoazobenzene. This difference, however, is explained by the fact that *p*-nitroaniline gives rise to quinone derivatives, whereas *m*-nitroaniline does not: on reduction of *p*-nitroaniline to the corresponding hydroxylamine, this compound loses one molecule of water, yielding quinone di-imide:

$$\underset{p\text{-Nitroaniline}}{NH_2\cdot C_6H_4\cdot NO_2} \rightarrow \underset{p\text{-Aminophenylhydroxylamine}}{NH_2\cdot C_6H_4\cdot NHOH} \rightarrow \underset{\text{Quinone di-imide}}{NH:C_6H_4:NH.}$$

The di-imide can be reduced to *p*-phenylenediamine:

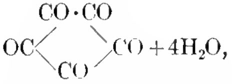
$$NH:C_6H_4:NH+2H = \underset{p\text{-Phenylenediamine}}{H_2N\cdot C_6H_4\cdot NH_2.}$$

m-Nitroaniline is unable to form a quinone derivative, and is, therefore, reduced normally in accordance with the scheme



$$C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}NHOH\\NH_2\end{matrix} + C_6H_4<\begin{matrix}NO\\NH_2\end{matrix} = \begin{array}{ccccc}C_6H_4\cdot N & — & — & — & N\cdot C_6H_4\\ | & \diagdown & O & \diagup & | \\ NH_2 & & & & NH_2\end{array} + H_2O.$$

358. Pentamethylene yields remarkable quinones, obtained by the oxidation of hexahydroxybenzene in alkaline solution. Among them is *croconic acid*, $C_5H_2O_5$, which has an intense yellow colour, and is converted by weak reducing agents into a colourless substance, oxidizable to croconic acid. On oxidation, croconic acid is transformed into *leuconic acid*, $C_5O_5+4H_2O$. This compound has the constitution

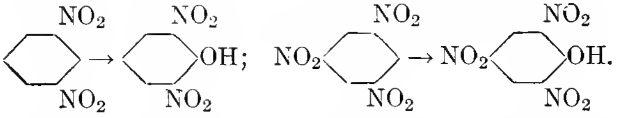


since it yields a pentoxime of the formula $(C:NOH)_5$.

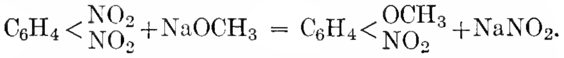
V. POLYNITRO-DERIVATIVES.

359. m-*Dinitrobenzene* is obtained by the nitration of benzene with a mixture of concentrated sulphuric acid and fuming nitric acid. It forms colourless needles melting at 90°. On reduction, it yields m-*phenylenediamine*, and is therefore employed in the preparation of aniline dyes: it is also used in the manufacture of explosives, since it can be exploded by mercury fulminate. In addition to the *m*-compound, small quantities of o-*dinitrobenzene* and traces of p-*dinitrobenzene* are formed. Stronger nitration, effected by a mixture of nitric acid and fuming sulphuric acid heated to 140°, converts *m*-dinitrobenzene into *symmetrical trinitrobenzene* (1:3:5), which melts at 121°.

The hydrogen atoms and nitro-groups in the polynitrobenzenes are much more readily replaced than those in mononitrobenzene. Thus, *m*-dinitrobenzene is converted by oxidation into 2:6-*dinitrophenol*, and trinitrobenzene into 2:4:6-trinitrophenol, or *picric acid:*



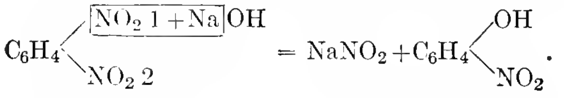
By the action of sodium ethoxide and methoxide respectively one of the nitro-groups in *o*-dinitrobenzene and *p*-dinitrobenzene can be replaced by OC_2H_5 and OCH_3:



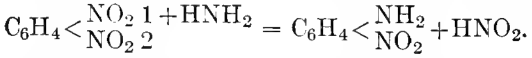
$$C_6H_4 < \begin{matrix}NO_2\\ NO_2\end{matrix} + NaOCH_3 = C_6H_4 < \begin{matrix}OCH_3\\ NO_2\end{matrix} + NaNO_2.$$

It is remarkable that this substitution does not take place with *m*-dinitrobenzene.

When boiled with caustic soda, *o*-dinitrobenzene yields o-*nitrophenol*, and when heated with alcoholic ammonia, o-*nitroaniline:*



$$C_6H_4 \begin{matrix}\boxed{NO_2\,1 + Na}OH\\ NO_2\,2\end{matrix} = NaNO_2 + C_6H_4 \begin{matrix}OH\\ NO_2\end{matrix}.$$



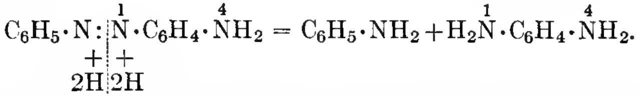
$$C_6H_4 < \begin{matrix}NO_2\,1\\ NO_2\,2\end{matrix} + HNH_2 = C_6H_4 < \begin{matrix}NH_2\\ NO_2\end{matrix} + HNO_2.$$

Trinitrobutylxylene, containing a tertiary butyl-group, has an odour resembling musk. It is a perfume, and is called "artificial musk."

VI. POLYAMINO-COMPOUNDS AND THEIR DERIVATIVES.

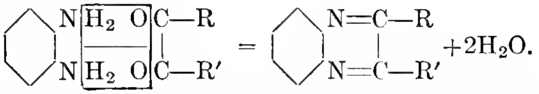
360. *Polyamino-compounds* are obtained by the reduction of polynitro-derivatives. m-*Phenylenediamine*, $C_6H_4{<}\begin{matrix}NH_2\ 1\\ NH_2\ 3\end{matrix}$, is got from benzene by nitration and subsequent reduction.

p-*Phenylenediamine* can be prepared by the reduction of amino-azobenzene (**343**) with tin and hydrochloric acid, aniline being also formed:



$$C_6H_5\cdot N:\overset{1}{N}\cdot C_6H_4\cdot\overset{4}{N}H_2 = C_6H_5\cdot NH_2 + H_2\overset{1}{N}\cdot C_6H_4\cdot\overset{4}{N}H_2.$$
$$\begin{matrix}+ & +\\ 2H & 2H\end{matrix}$$

Ortho-diamino-compounds react readily with 1:2-diketones, yielding *quinoxalines:*



Like the polyhydric phenols, the polyamino-compounds are very readily oxidized. They are colourless, but many of them are turned brown by oxidation in the air.

Azo-dyes.

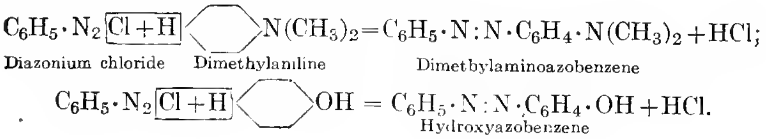
361. The azo-derivatives of the polyamino-compounds are known as *azo-dyes.* They are of great technical importance, being extensively employed in dyeing wool, silk, and cotton. They are azobenzenes in which hydrogen atoms have been replaced by amino-groups. They are not the only dyes: derivatives of azobenzene with hydrogen replaced by hydroxyl or by the sulpho-group can likewise be employed in dyeing. Some of these compounds will also be described.

It is necessary first to state certain facts regarding dyes in general. It has been proved by experiment that not every colouring-matter can dye the substances named above; that is, colour them so that the dye cannot subsequently be removed by rubbing, or washing with water or soap. It is necessary, therefore, to draw a distinction between coloured substances and dyes: for example, azobenzene has a deep yellowish-red colour, but is not a dye. The introduction of an amino-group, however, converts it into a dye, aminoazobenzene. Witt has propounded the theory that the colouring-power of a compound depends upon two factors. The first of these is the presence of certain groups, which he calls *chromophores,* among them being the azo-group, —N=N—, the nitro-group, and others. Substances containing a chromophore-group, along with NH_2, OH, SO_3H, or in general any group which imparts to them an acidic or basic character, are dyes: this is illustrated by aminoazobenzene. Another example is nitrobenzene, which has a pale-yellow colour, and contains the chromophore nitro-group, but is not a dye: on the other hand, *p*-nitroaniline and *p*-nitrophenol are dyes.

362. It is often sufficient to immerse the silk, wool, or cotton to be dyed in a solution of the dye. Although primarily dissolved, the dye cannot be removed by washing the fabric after dyeing. The dye must, therefore, have undergone a change. It is assumed that it unites with the constituents of the animal or vegetable fibres to form a compound, a kind of salt, since dyes always have a basic or acidic character. A proof of this is given for rosaniline (426).

The fabric does not always take up the dye when immersed in its solution. It has been repeatedly observed that dyes which become directly fixed on animal fabrics, such as silk and wool, do not dye vegetable fabrics, like cotton, unless the material to be dyed has undergone a special process, called "mordanting": that is, a substance must be deposited in the fabric to "fix" the dye, since it will not unite with the fibres themselves. Such substances are called "mordants": they are usually salts of weak bases, or acids. Such are aluminium acetate; ferric salts; compounds of tin, such as "pink salt," $SnCl_4, 2NH_4Cl$. The woven material is thoroughly soaked in a solution of one of these salts, and then spread out and exposed to the action of steam at a suitable temperature. The salt undergoes hydrolytic dissociation, and the base or acid, for example aluminium hydroxide or stannic acid, is deposited in a fine state of division in the fabric. The dye unites with this base or acid, forming an insoluble, coloured compound which is not removed by washing.

363. Azo-dyes are obtained by treating diazonium chlorides with aromatic amines or with phenols:



Basic and acidic dyes respectively are produced. It is mentioned in **343** that the combination of a diazonium chloride and an aromatic amine sometimes yields the diazoamino-compound as an intermediate product, which can be converted into the aminoazo-derivative by warming with the amine hydrochloride. In this formation of aminoazo-compounds and hydroxyazo-compounds, the *para*-H-atom always reacts with the diazonium chloride: when this atom is replaced by a substituent, the formation of dye either does not take place, or is very incomplete.

364. In preparing hydroxyazo-dyes, the solution of the diazonium chloride is cooled with ice, and is slowly added to the *alkaline* solution of the phenol or its sulphonic acid. The reaction-mixture is kept slightly alkaline, since otherwise the hydrochloric acid liberated would hinder the formation of the dye. After the solutions have been mixed, the dye is "salted out" by the addition of common salt, which precipitates it in flocculent masses. It is freed from water by means of filter-presses, and packed either as a powder or a paste.

Aminoazo-dyes are prepared by mixing the aqueous solution of the diazonium chloride with that of the aromatic amine salt, the colouring-matter being subsequently salted out. It is sometimes necessary to employ an alcoholic solution.

The simplest azo-dyes are yellow. The introduction of alkyl-groups or phenyl-groups, and, in general, increase of molecular weight, change their colour through orange and red to violet and blue. They are crystalline, and most of them are insoluble in water and soluble in alcohol. Instead of the azo-dyes themselves, it is often better to employ their sulphonic acids, obtainable from them by the usual method—treatment with concentrated sulphuric acid.

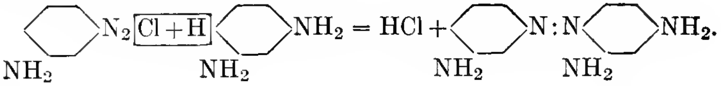
365. *Aniline-yellow* is a salt of aminoazobenzene: it is seldom used now, its place having been taken by other yellow dyes.

Chrysoïdine or diaminoazobenzene, $C_6H_5\cdot N{:}N\cdot C_6H_3{<}\begin{matrix}NH_2\\NH_2\end{matrix}$, is obtained from benzenediazonium chloride and *m*-phenylenediamine. It yields a hydrochloride, crystallizing in needles of a reddish colour and fairly soluble in water: this salt dyes wool and silk directly and cotton which has been mordanted.

Bismarck-brown or triaminoazobenzene,

$$NH_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_3{<}\begin{matrix}NH_2\\NH_2\end{matrix},$$

is manufactured by diazotizing one of the NH_2-groups in *m*-phenylenediamine, and treating the product thus obtained with a second molecule of this base:



Even a very dilute solution of nitrous acid gives a brown coloration with *m*-phenylenediamine, due to the formation of Bismarck-brown or related substances. This reaction furnishes a very delicate test for nitrous acid, and is employed in water-analysis.

Helianthine, or dimethylaminoazobenzenesulphonic acid, is prepared by the interaction of benzenediazoniumsulphonic acid and dimethylaniline hydrochloride in aqueous solution:

$$HO_3S \cdot C_6H_4 \cdot N_2\boxed{OH + H}C_6H_4 \cdot N(CH_3)_2 =$$

$$= H_2O + \underset{\text{Helianthine}}{HO_3S \cdot C_6H_4 \cdot N:N \cdot C_6H_4 \cdot N(CH_3)_2}.$$

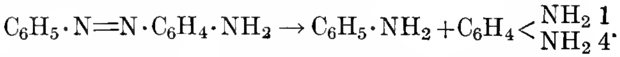
It is not often used as a dye, but its sodium salt, which has a yellow colour, and is turned red by acids, is employed as an indicator in volumetric analysis under the name *methyl-orange*.

Resorcin-yellow or dihydroxyazobenzenesulphonic acid,

$$HO_3S \cdot C_6H_4 \cdot N:N \cdot C_6H_3 < \begin{matrix} OH \\ OH \end{matrix},$$

is obtained from resorcinol (**353**) and benzenediazonium sulphonic acid.

The azo-dyes are converted into amino-compounds by energetic reduction with tin and hydrochloric acid. Thus, aminoazobenzene yields aniline and *p*-phenylenediamine:



$$C_6H_5 \cdot N{=}N \cdot C_6H_4 \cdot NH_2 \rightarrow C_6H_5 \cdot NH_2 + C_6H_4 < \begin{matrix} NH_2 \; 1 \\ NH_2 \; 4 \end{matrix}.$$

This decomposition on reduction affords a means of determining the constitution of these dyes, and indicates the methods by which they are obtained. For example, reduction of Bismarck-brown with tin and hydrochloric acid yields a mixture of equimolecular amounts of diaminobenzene and triaminobenzene. Since the molecule is severed at the double linking of the azo-group, it follows that the constitution of this compound is

$$NH_2 \cdot C_6H_4—N:\vdots N—C_6H_3<\genfrac{}{}{0pt}{}{NH_2}{NH_2}.$$

This decomposition also indicates that the dye can be obtained by diazotizing a molecule of diaminobenzene, and treating the product with a second molecule of diaminobenzene, in accordance with the equation on the previous page.

VII. POLYBASIC ACIDS AND THEIR DERIVATIVES.

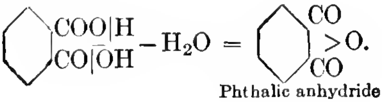
DIBASIC ACIDS.

366. The dibasic acids are the most important members of the series of aromatic polybasic acids. They are called *phthalic acids*, a name derived from na*phthal*ene (431), from which one of them can be obtained. Three isomerides are possible, and all of them are known. Like all polybasic acids, they yield neutral and acid esters and salts, acid amides, amino-acids, etc. On distillation with lime, they are converted into benzene.

Phthalic Acid.

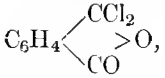
367. *Phthalic acid* is the *ortho*-dicarboxylic acid of benzene, and has the formula $C_6H_4<\genfrac{}{}{0pt}{}{COOH\ 1}{COOH\ 2}$. It is obtained by the oxidation of aromatic hydrocarbons with two side-chains in the *ortho*-position, or their derivatives with substituents in the side-chains. It is worthy of note that chromic acid cannot be employed in this oxidation, since it decomposes *ortho*-derivatives completely into carbon dioxide and water. Phthalic acid is employed in the preparation of artificial indigo (469), and is manufactured by oxidizing naphthalene (431), $C_{10}H_8$, by heating with very concentrated sulphuric acid.

Phthalic acid is crystalline, and dissolves readily in hot water, alcohol, and ether. It has no definite melting-point, since on heating it loses water, yielding *phthalic anhydride*, which sublimes in beautiful, long needles:



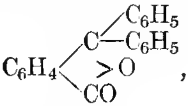
Phthalic anhydride

368. If they followed the ordinary course of the reaction forming acid chlorides, phosphorus pentachloride and phthalic acid would react to produce a chloride of the constitution $C_6H_4<\begin{smallmatrix}COCl\\COCl\end{smallmatrix}$. That they do not and that *phthalyl chloride* has the structure



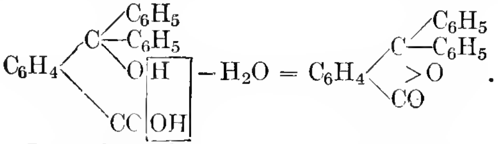
$$C_6H_4\begin{smallmatrix}/CCl_2\\ \\ \backslash CO\end{smallmatrix}>O,$$

can be proved in various ways. When aluminium chloride reacts with phthalyl chloride in presence of benzene, there results a compound with the formula



$$C_6H_4\begin{smallmatrix}/C\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}\\ \\ \backslash CO\end{smallmatrix}>O,$$

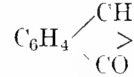
called *phthalophenone*, the constitution of which follows from its formation by the elimination of water from *triphenylcarbinolcarboxylic acid:*

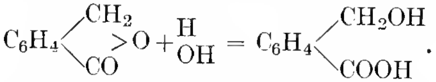


$$C_6H_4\begin{smallmatrix}/C\begin{smallmatrix}C_6H_5\\C_6H_5\\O\boxed{H}\end{smallmatrix}\\ \\ \backslash CO\boxed{OH}\end{smallmatrix}-H_2O=C_6H_4\begin{smallmatrix}/C\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}\\ \\ \backslash CO\end{smallmatrix}>O.$$

Triphenylcarbinol-carboxylic acid

Phthalophenone

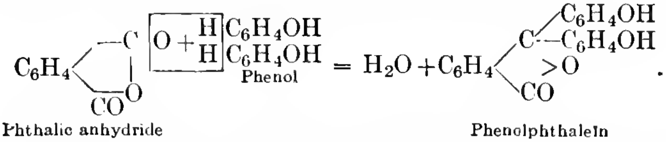
Another proof of the constitution indicated above for phthalyl chloride is the fact that reducing agents, such as sodium-amalgam and water, or zinc and hydrochloric acid, cause the replacement of its halogen atoms by hydrogen, with formation of *phthalide.* This substance has the constitution  $C_6H_4\begin{smallmatrix}/CH_2\\ \\ \backslash CO\end{smallmatrix}>O$, since on treatment with caustic soda or dilute acids it yields *hydroxymethylbenzoic acid:*



$$C_6H_4\begin{smallmatrix}/CH_2\\ \\ \backslash CO\end{smallmatrix}>O+\begin{smallmatrix}H\\OH\end{smallmatrix}=C_6H_4\begin{smallmatrix}/CH_2OH\\ \\ \backslash COOH\end{smallmatrix}.$$

This reaction proves it to be a lactone, and not a dialdehyde, $C_6H_4<\begin{smallmatrix}CHO\\CHO\end{smallmatrix}$, as it should be if the formula of phthalyl chloride were $C_6H_4<\begin{smallmatrix}COCl\\COCl\end{smallmatrix}$.

369. The oxygen of the carbonyl-group in phthalic anhydride can also participate in other reactions. Thus, when this substance is heated with phenols and sulphuric acid, *phthaleïns* are formed:

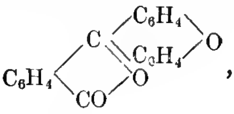


Phenolphthaleïn, the simplest member of the phthaleïn series, is a yellow powder. On account of its phenolic character it dissolves in alkaline solutions, with formation of a fine red colour, and is a sensitive indicator for alkalimetry.

Resorcinolphthaleïn or *fluoresceïn* is characterized by the display of an intense yellowish-green fluorescence in alkaline solution. It owes its name to this property, which affords a delicate test for phthalic anhydride, phthalic acid, and resorcinol, since fluorescence is exhibited by mere traces of fluoresceïn. It is prepared by heating together resorcinol and phthalic anhydride at 210°, in presence of zinc chloride as a dehydrating agent. On treatment with bromine, fluoresceïn yields *tetrabromofluoresceïn:* its potassium derivative, $C_{20}H_6O_5Br_4K_2$, is the beautiful dye *eosin*.

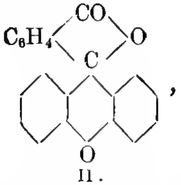
The constitution of the phthaleïns is inferred from their being convertible into derivatives of triphenylmethane (**423**).

370. In the preparation of the phenolphthaleïn a by-product, *fluoran*, insoluble in alkalis is formed. According to the researches of R. MEYER, this substance has the formula



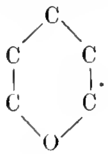
I.

or

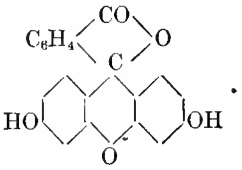


II.

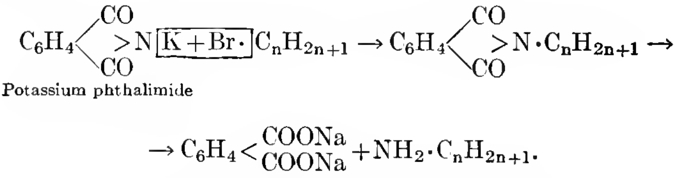
in which the two phenol-residues are united at the *ortho*-positions to the phthalic-anhydride-residue, and not at the *para*-positions, as in phenolphthaleïn. Fluoran contains the pyrone-nucleus,



R. Meyer has pointed out that many derivatives containing this nucleus fluoresce. He proved that fluoresceïn is dihydroxyfluoran, with the formula



371. *Phthalimide*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NH$, is of importance on account of its application by Gabriel to the synthesis of primary amines with substituted alkyl-groups. It is obtained by passing dry ammonia over heated phthalic anhydride. The imino-hydrogen is replaceable by metals: thus, the potassium compound is precipitated by the action of caustic potash upon the alcoholic solution of the imide. When *potassium phthalimide* is treated with an alkyl halide, the metal is replaced by alkyl: on heating with acids or alkalis, a primary amine, free from secondary and tertiary amines, is produced:



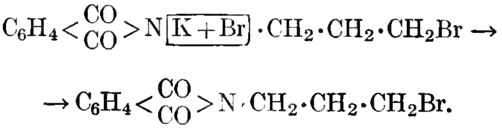
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\boxed{K+Br\cdot}C_nH_{2n+1} \rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_nH_{2n+1} \rightarrow$$

Potassium phthalimide

$$\rightarrow C_6H_4<\begin{matrix}COONa\\COONa\end{matrix}+NH_2\cdot C_nH_{2n+1}.$$

Alkyl halides with various substituents can be employed in this reaction: thus, from ethylene bromide, $CH_2Br\cdot CH_2Br$, is obtained *bromoethylamine*, $NH_2\cdot CH_2\cdot CH_2Br$; from ethylenebromohydrin, $CH_2Br\cdot CH_2OH$, *hydroxyethylamine*, $NH_2\cdot CH_2\cdot CH_2OH$; etc.

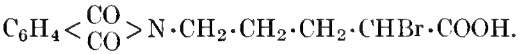
Another example is Emil Fischer's synthesis of *ornithine* (**231**). Potassium phthalimide is brought into contact with trimethylene bromide:



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\boxed{K+Br}\cdot CH_2\cdot CH_2\cdot CH_2Br \rightarrow$$

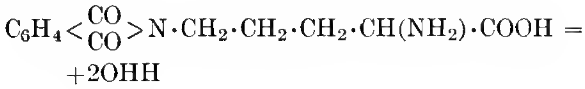
$$\rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot CH_2Br.$$

The compound obtained is treated with diethyl monosodiomalonate, and yields $C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOC_2H_5)_2$, the tertiary hydrogen atom of which can be substituted by bromine. Saponification and elimination of CO_2 give

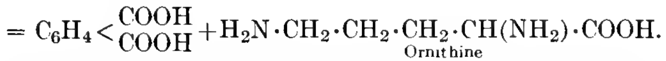


$$C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHBr\cdot COOH.$$

By heating with aqueous ammonia, Br is then replaced by NH_2. Subsequent heating with concentrated hydrochloric acid yields ornithine:



$$C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH = \\ +2OHH$$

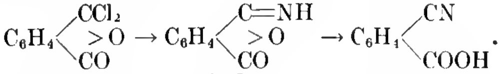


$$= C_6H_4<\substack{COOH\\COOH}+\underset{\text{Ornithine}}{H_2N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH}.$$

Ornithine

These examples make it evident that this method can be applied to the preparation of the most variously substituted primary amines.

372. HOOGEWERFF and VAN DORP found that ammonia reacts with phthalyl chloride, yielding *o-cyanobenzoïc acid*, $C_6H_4<\substack{CN\\COOH}$. It must be assumed that an iso-*imide* of phthalic acid is formed as an intermediate product:



Phthalyl chloride
iso-Imide
o-Cyanobenzoïc acid

Although they have not been able to isolate the *iso*-imide itself, they have prepared a number of derivatives in which the imino-hydrogen is replaced by hydrocarbon-residues.

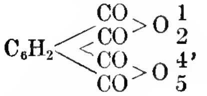
*iso*Phthalic and Terephthalic Acids, $C_6H_4(COOH)_2$ (1:3) and (1:4).

373. iso*Phthalic acid* can be obtained by the oxidation of compounds with two side-chains in the *meta*-position, and also by the oxidation of resin (colophonium) with nitric acid. It dissolves with difficulty in water, and does not yield an anhydride.

Terephthalic acid can be prepared by several methods; for example, by the oxidation of turpentine. It is almost insoluble in water, alcohol, and ether. It does not melt at the ordinary pressure, but at high temperatures sublimes without decomposition. Like *iso*-phthalic acid, it does not form an anhydride.

HIGHER POLYBASIC ACIDS.

374. Tricarboxylic, tetracarboxylic, pentacarboxylic, and hexacarboxylic acids are known. The most remarkable is the hexacarboxylic *mellitic acid*, a constituent of the mineral *honey-stone*, found in brown-coal seams. Honey-stone is the aluminium salt of mellitic acid, and has the formula $C_{12}O_{12}Al_2 + 18H_2O$: it forms yellow quadratic octahedra. Mellitic acid is produced by the oxidation of wood-charcoal with an alkaline solution of potassium permanganate. It crystallizes in fine needles, and dissolves freely in water and alcohol. On heating, it loses two molecules of carbon dioxide and two molecules of water, with formation of *pyromellitic anhydride*,



$$C_6H_2\left\langle\begin{array}{l}\left.\begin{array}{l}CO\\CO\end{array}\right>O\;\begin{array}{l}1\\2\end{array}\\\left.\begin{array}{l}CO\\CO\end{array}\right>O\;\begin{array}{l}4,\\5\end{array}\end{array}\right.$$

which takes up water, and yields *pyromellitic acid*, $C_6H_2(COOH)_4$.

DERIVATIVES WITH TWO OR MORE DISSIMILAR SUBSTITUENTS.

I. SULPHO-DERIVATIVES.

Halogensulphonic Acids.

375. Among the *halogensulphonic acids* are the three *bromobenzenesulphonic acids.* On fusion with caustic potash each yields resorcinol, $C_6H_4<^{OH\ 1}_{OH\ 3}$. This reaction exemplifies a comparatively rare phenomenon—the introduction of a substituent into a position other than that occupied by the group replaced. Similar examples are cited in 379 and 398.

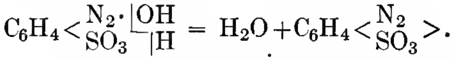
Phenolsulphonic Acids.

376. o-*Phenolsulphonic acid* and p-*phenolsulphonic acid* are obtained by dissolving phenol in concentrated sulphuric acid. m-*Phenolsulphonic acid* is produced by fusing *m*-benzenedisulphonic acid with caustic potash. The *o*-acid is characterized by being easily converted into the *p*-compound, even on evaporation of its aqueous solution. Phenol sulphonates more readily than benzene, its solution in sulphuric acid being transformed into the *o*-sulpho-acid and *p*-sulpho-acid even at ordinary temperatures.

p-Aminobenzenesulphonic Acid or Sulphanilic Acid.

377. *Sulphanilic acid* is obtained by heating aniline with fuming sulphuric acid. Like its isomerides, it dissolves with difficulty in cold water. The basic properties of aniline are greatly weakened by the introduction of the sulpho-group into the ring, for sulphanilic acid cannot yield salts with acids, whereas the sulpho-group reacts

with bases, forming salts. The formula of sulphanilic acid is probably $C_6H_4<\genfrac{}{}{0pt}{}{SO_3}{NH_3}>$; that is, it is an inner salt. On fusion with caustic potash, it does not yield aminophenol, in accordance with precedent, but aniline. Oxidation with chromic acid converts it into quinone. On pouring a mixture of sodium sulphanilate and sodium nitrite in aqueous solution into dilute sulphuric acid, an inner salt of *benzenediazoniumsulphonic acid* is precipitated, being nearly insoluble in water:

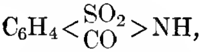


$$C_6H_4<\genfrac{}{}{0pt}{}{N_2\cdot|OH}{SO_3\;\;|H} = H_2O + C_6H_4<\genfrac{}{}{0pt}{}{N_2}{SO_3}>.$$

This compound is of great importance in the preparation of azo-dyes, such as *helianthine* (365).

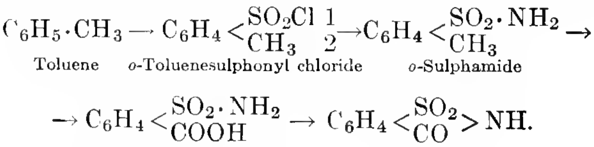
Sulphobenzoïc Acids.

378. o-*Benzoïc sulphinide*,



$$C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{CO}>NH,$$

the imino-derivative of *o*-sulphobenzoïc acid, is known as "saccharin." It is about three hundred times as sweet as sugar, and on this account is sometimes employed as a substitute for it. Direct sulphonation of benzoïc acid yields m-*sulphobenzoïc acid* almost exclusively, so that saccharin cannot be prepared by this means. It is obtained from toluene, which, on treatment with chlorosulphonic acid, $SO_2(OH)Cl$, yields a mixture of p-*toluenesulphonyl chloride* and o-*toluenesulphonyl chloride*, the former being the chief product. The *o*-chloride is converted into its *sulphamide*, the methyl-group of which is then transformed into carboxyl by oxidation with potassium permanganate. On heating, this oxidation-product loses one molecule of water very readily, forming saccharin:



$$C_6H_5\cdot CH_3 \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{SO_2Cl}{CH_3}\genfrac{}{}{0pt}{}{1}{2}\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{SO_2\cdot NH_2}{CH_3}\rightarrow$$

Toluene *o*-Toluenesulphonyl chloride *o*-Sulphamide

$$\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{SO_2\cdot NH_2}{COOH}\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{CO}>NH.$$

o-Sulphamide of benzoïc acid Saccharin

Saccharin is a white, crystalline powder, soluble with difficulty in cold water, and readily soluble in alcohol and ether. It takes up one molecule of water, yielding the sulphamide of *o*-sulphobenzoïc acid, which does not possess a sweet taste.

REMSEN found that the "saccharin" of commerce is a mixture of *o*-benzoïc sulphinide; p-*sulphaminobenzoic acid*, $COOH \cdot C_6H_4 \cdot SO_2NH_2$; and *potassium hydrogen* o-*sulphobenzoate*, $COOH \cdot C_6H_4 \cdot SO_2OK$, containing less than fifty per cent. of the sulphinide. The melting-point of the pure sulphinide is 220°.

II. HALOGEN DERIVATIVES.

Halogenphenols.

379. o-*Chlorophenol* and p-*chlorophenol* are formed by the direct chlorination of phenol, and also by reduction of the halogen-nitrobenzenes and subsequent diazotization of the compounds formed. They have a pungent odour. By fusion with caustic potash, the halogen can be replaced by hydroxyl, although the corresponding hydroxyl-compound is not always formed (375). The introduction of halogen considerably augments the acidic character of the phenols: thus, trichlorophenol decomposes carbonates. It is mentioned in 303 that the presence of hydroxyl in the ring considerably facilitates the substitution of the hydrogen atoms by halogen. Iodine, however, can only substitute in presence of an oxidizing agent, to remove the hydriodic acid formed; since, unless this were oxidized, it would remove the iodine atom from the iodophenol produced.

Halogenbenzoïc Acids.

380. m-*Chlorobenzoïc acid* can be obtained by direct chlorination of benzoïc acid, but is most readily got by diazotizing the corresponding amino-compound, which is also the best method for the preparation of the *ortho*-halogenbenzoïc and *para*-halogenbenzoïc acids. Phosphorus pentachloride does not react readily with the hydroxybenzoïc acids; hence the halogenbenzoïc acids cannot be satisfactorily prepared by its aid.

As would be expected, the acidic character of benzoïc acid is strengthened by the introduction of halogen. The dissociation-constant 10^4k of the halogenbenzoïc acids is greater than that of benzoïc acid itself. For benzoïc acid 10^4k is $0 \cdot 6$; for *o*-chlorobenzoïc acid 13·2; for *m*-chlorobenzoïc acid 1·55; for *p*-chlorobenzoïc acid 0·93. These values prove that the chlorine atom in the *ortho*-position exercises the greatest influence and that in the *para*-position the least, while for the *m*-compound 10^4k is intermediate in value.

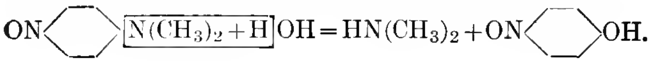
Compounds containing halogen and the sulpho-group are referred to in 375.

III. HYDROXYL-DERIVATIVES.

Nitrosophenol.

381. In certain respects *nitrosophenol* reacts as though it had the constitution $C_6H_4<\genfrac{}{}{0pt}{}{NO}{OH}$, although its formation from quinone and hydroxylamine points to the constitution $C_6H_4\genfrac{}{}{0pt}{}{\diagup NOH}{\diagdown O}$. It is prepared by the action of nitrous acid upon phenol, or of caustic potash upon nitrosodimethylaniline:

$$C_6H_4<\genfrac{}{}{0pt}{}{\boxed{H+HO}NO}{OH} = C_6H_4<\genfrac{}{}{0pt}{}{NO}{OH}+H_2O;$$

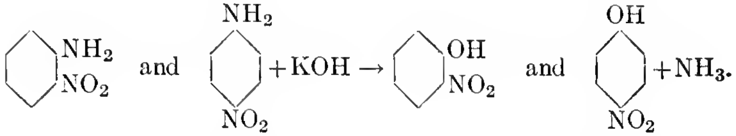


Like other oximes, nitrosophenol, or quinone mono-oxime, unites with bases. It is a colourless compound, crystallizing in needles which soon turn brown on exposure to air. On oxidation and reduction, it behaves as though it were nitrosophenol, yielding nitrophenol and aminophenol respectively.

Nitrophenols.

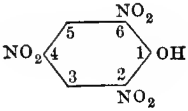
382. The increased aptitude for substitution displayed by the hydrogen atoms of the benzene-nucleus after introduction of a hydroxyl-group is illustrated by the behaviour of the phenols towards nitric acid. To obtain nitrobenzene from benzene, it is necessary to employ concentrated nitric acid, whereas phenol is converted by dilute nitric acid at low temperatures into *o*-nitrophenol and *p*-nitrophenol. The two isomerides can be separated by distillation with steam, with which only the *ortho*-compound is volatile. m-*Nitrophenol* can be prepared from *m*-nitroaniline by

the diazo-reaction. *o*-Nitroaniline and *p*-nitroaniline, but not *m*-nitroaniline, yield nitrophenols directly by fusion with potash:



This reaction proves that the presence of several substituents in the benzene-nucleus considerably facilitates the introduction of other groups. The acidic character of phenol is strengthened in the nitrophenols: they decompose all carbonates, although nitrophenol is precipitated from a solution of an alkali-metal nitrophenoxide by carbon dioxide.

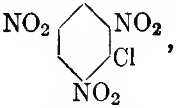
383. The most important nitrophenol derivative is *picric acid,* or 1:2:4:6-trinitrophenol,



This substance has been known for a long time, and is produced by the action of concentrated nitric acid upon many substances, such as silk, leather, resins, aniline, indigo, etc. It is prepared by dissolving phenol in concentrated sulphuric acid, and carefully adding small quantities of this solution to concentrated nitric acid of 1·4 specific gravity. An energetic reaction ensues, after which the mixture is warmed for some time on a water-bath: on cooling, picric acid crystallizes out. It cannot be further nitrated: in other words, it is the final product of the action of nitric acid upon phenol. This fact explains its production by the action of nitric acid upon such heterogeneous substances.

When pure, solid picric acid has only a very faint-yellow colour, but its aqueous solution is deep yellow. It is a strong acid, and, therefore, undergoes considerable ionization on solution in water: the yellow colour is characteristic of the anion, since the solution of this acid in petroleum-ether, in which there is no ionization, is colourless. It is slightly soluble in cold water, and is not volatile with steam. It melts at 122°.

A consideration of the following reactions shows that picric acid is comparable with the carboxylic acids. Phosphorus pentachloride replaces the hydroxyl-group by chlorine, with formation of *picryl chloride*,



which has the character of an acid chloride. Thus, it is decomposed by hot water into hydrochloric acid and picric acid, and with ammonia yields *picramide*, $C_6H_2\begin{matrix}(NO_2)_3 & 2:4:6 \\ NH_2 & 1\end{matrix}$. Silver picrate and methyl iodide yield *methyl picrate:* it has the properties of an ester, being saponified by boiling with concentrated caustic alkalis, and yielding picramide on treatment with ammonia. These facts afford further evidence of the remarkable increase in the reactivity of the hydroxyl-group, due to the presence of the three nitro-groups.

Picric acid yields well-defined crystalline, explosive salts, of a yellow or red colour. The potassium salt dissolves with difficulty in water, and the ammonium salt explodes by percussion, although the acid itself does not.

It yields molecular compounds with many aromatic hydrocarbons; for example, with naphthalene a compound of the formula $C_{10}H_8 \cdot C_6H_2(NO_2)_3 \cdot OH$. These derivatives crystallize well, and have definite melting-points. They are sometimes employed with advantage in the separation of hydrocarbons, or in their identification. Picric acid is eliminated from them by the action of ammonia.

The acid can be detected by an aqueous solution of potassium cyanide, which yields a red coloration due to the formation of *iso*purpuric acid.

Picric acid is employed as an explosive, which leaves no residue on explosion, and is called "lyddite." It is also used as a dye, imparting a yellow colour to wool and silk.

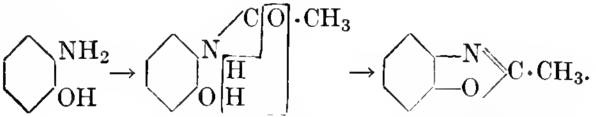
384. *Styphnic acid*, $C_6H\begin{matrix}(OH)_2 \\ (NO_2)_3\end{matrix}$ is a type of a nitrated dihydroxybenzene, and is obtained by the action of cold nitric acid upon resorcinol, as well as from certain gum-resins by the same means. The conversion of *m*-nitrophenol into styphnic acid by the action of

nitric acid involves the intermediate formation of a tetranitro-compound, in which one of the nitro-groups is so reactive as to be replaceable by hydroxyl on treatment with water, with formation of styphnic acid.

Aminophenols.

385. *Aminophenols* are formed by the reduction of nitrophenols. The acidic character in these compounds is so weakened that they do not combine with bases: on the other hand, they yield salts with acids. In the free state the aminophenols are colourless solids, crystallizing in leaflets, and readily turned brown by atmospheric oxidation with formation of a resin. Their hydrochlorides are more stable.

o-*Aminophenol* yields compounds by the substitution of acid-residues in the amino-group, which at once lose water, forming *anhydro-bases:*



Acetyl-derivative

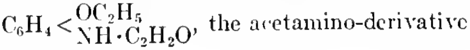
Ethenylaminophenol,
Anhydro-base

On treatment with acids, aminophenol and acetic acid are regenerated.

p-*Aminophenol* is obtained by the electro-reduction of nitrobenzene in acid solution (326).

The alkaline solution of *p*-aminophenol rapidly acquires a dark colour, unless sodium sulphite is present. The trade-name of this solution is "rodinal." It finds application as a photographic developer.

LUMIÈRE has discovered certain general conditions which aromatic compounds must fulfil to be available as photographic developers. They must either contain some hydroxyl-groups or amino-groups, or at least one of each class. In order that the developing action may not be interfered with when substituents are present in the amino-group and in the hydroxyl-group, not less than two such unsubstituted groups must be present in the molecule.

A derivative of *p*-aminophenol used in medicine is "phenacetin" or *acetylphenetidine*,  $C_6H_4<\begin{matrix}OC_2H_5\\NH\cdot C_2H_2O\end{matrix}$, the acetamino-derivative of phenetole, $C_6H_5\cdot OC_2H_5$.

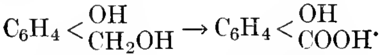
Salts of 1:2:4-diaminophenol are employed as photographic developers under the name "amidol."

Monohydroxy-acids.

386. The most important of the monohydroxy-acids is *o*-hydroxybenzoic acid, or *salicylic acid*, $C_6H_4<\begin{matrix}OH & 1\\ COOH & 2\end{matrix}$. It derives its name from salicin, a glucoside in the bark and leaves of the willow (*salix*). On hydrolysis, this substance yields *saligenin* and dextrose:

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7}+H_2O=\underset{\text{Saligenin}}{C_7H_8O_2}+\underset{\text{Dextrose}}{C_6H_{12}O_6}.$$

Saligenin is the alcohol corresponding to salicylic acid, into which it is converted by oxidation:



$$\underset{\text{Saligenin}}{C_6H_4<\begin{matrix}OH\\ CH_2OH\end{matrix}}\rightarrow\underset{\text{Salicylic acid}}{C_6H_4<\begin{matrix}OH\\ COOH\end{matrix}}.$$

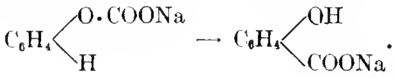
Salicylic acid is present as methyl ester in oil of wintergreen (*Gaultheria procumbens*), from which the acid is sometimes obtained for pharmaceutical use. It can also be prepared by the action of nitrous acid on anthranilic acid, *o*-aminobenzoïc acid (397), by fusing *o*-chlorobenzoïc acid or *o*-bromobenzoïc acid with caustic potash, and by other methods.

Salicylic acid is manufactured by a process discovered by KOLBE and improved by SCHMIDT, in which sodium phenoxide is heated with carbon dioxide in an autoclave at 130°.

At the ordinary temperature at a pressure of about 1½ atmospheres, sodium phenoxide and carbon dioxide react to form *sodium phenylcarbonate:*

$$C_6H_5\cdot O\cdot Na+CO_2=C_6H_5\cdot O\cdot COONa.$$

This compound is to be regarded as an intermediate product in the synthesis of salicylic acid. Its conversion into this substance is represented by the scheme

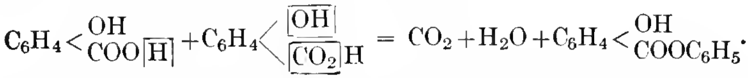


$$C_6H_4<\begin{matrix}O\cdot COONa\\ H\end{matrix}\longrightarrow C_6H_4<\begin{matrix}OH\\ COONa\end{matrix}.$$

Salicylic acid is a white, crystalline powder, which dissolves with difficulty in cold water, and melts at 159°. When carefully heated, it sublimes, but on rapid heating decomposes into phenol and carbon dioxide. With bromine-water it yields a precipitate of the formula $C_6H_2Br_3{\cdot}OBr$. It gives a violet coloration with ferric chloride, both in aqueous and in alcoholic solution, whereas phenol dissolved in alcohol does not. When boiled with calcium chloride and ammonia, a solution of salicylic acid precipitates basic calcium salicylate, $C_6H_4\begin{matrix}\diagup COO\diagdown\\ \diagdown O\diagup\end{matrix}Ca$: this reaction affords a means of separating salicylic acid from its isomerides, which do not give this reaction.

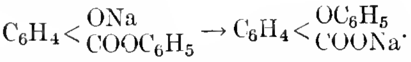
Salicylic acid is a powerful antiseptic, and is employed as a preservative for foods and such beverages as beer. It is not, however, completely innocuous. Sodium salicylate is employed as a medicine.

When the acid is heated to 220°, it loses carbon dioxide and water, with formation of *phenyl salicylate:*



$$C_6H_4<\begin{matrix}OH\\COO\boxed{H}\end{matrix}+C_6H_4<\begin{matrix}\boxed{OH}\\\boxed{CO_2}H\end{matrix}=CO_2+H_2O+C_6H_4<\begin{matrix}OH\\COOC_6H_5\end{matrix}.$$

This compound is employed as an antiseptic under the name "salol." By heating to 300°, its sodium derivative is converted into *sodium phenylsalicylate:*

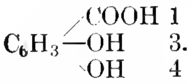


$$C_6H_4<\begin{matrix}ONa\\COOC_6H_5\end{matrix}\rightarrow C_6H_4<\begin{matrix}OC_6H_5\\COONa\end{matrix}.$$

m-*Hydroxybenzoïc acid* and p-*hydroxybenzoïc acid* yield no coloration with ferric chloride. Their basic barium salts are insoluble.

Dihydroxy-acids.

387. Among the *dihydroxy-acids* is *protocatechuic acid,*

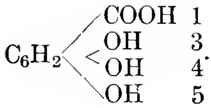


$$C_6H_3\begin{matrix}\diagup COOH & 1\\ -OH & 3.\\ \diagdown OH & 4\end{matrix}$$

It is obtained from many resins by fusion with potash, and synthetically by heating catechol with ammonium carbonate, the latter method being a striking example of the readiness with which the carboxyl-group can sometimes be introduced into the ring. It is freely soluble in water. It reduces an ammoniacal silver solution, but not an alkaline copper solution. It gives a characteristic reaction with ferric chloride, yielding a green colour, which changes to blue and finally to red on addition of a very dilute solution of sodium carbonate.

Trihydroxy-acids.

388. The best-known *trihydroxy-acid* is *gallic acid*,



$$C_6H_2\left\langle\begin{array}{ll}COOH & 1\\ OH & 3\\ OH & 4\\ OH & 5\end{array}\right.$$

It is a constituent of gall-nuts, tea, and "divi-divi," a material used in tanning. It is usually prepared by boiling tannin with dilute acids. It crystallizes in fine needles, readily soluble in hot water. It is mentioned in 354 that, on heating, the acid loses CO_2, forming pyrogallol. Gallic acid reduces the salts of gold and silver, and gives a bluish-black precipitate with ferric chloride. In alkaline solution it is turned brown in the air by oxidation, like pyrogallol.

Gallic acid is employed in the manufacture of blue-black ink. For this purpose its aqueous solution is mixed with a solution of ferrous sulphate containing a trace of free sulphuric acid. Without the acid, the ferrous sulphate would quickly oxidize in the air, giving a thick, black precipitate with the gallic acid: this oxidation is retarded in a remarkable manner by the addition of a very small quantity of sulphuric acid. As soon as the solution is brought into contact with paper, the free acid is neutralized by the alumina always present in the latter, and, as oxidation is no longer prevented, the writing in drying turns deep black. As the mixture of the solutions of ferrous sulphate and gallic acid has only a faint-brown colour, which would make the fresh writing almost invisible, indigo-carmine is added to the mixture. This imparts to the ink coming from the pen a dark-blue colour, which changes by the process described to a deep black.

389. The *tannins*, or *tannic acids*, are very closely related to gallic acid, and are widely distributed in the vegetable kingdom. The

tannins are compounds which are soluble in water, have a bitter, astringent taste, yield a dark-blue or green precipitate with ferric salts, convert substances containing gelatin—such as animal hides—into leather, and precipitate proteïns from their solutions. Some of the tannins are glucosides.

The most typical tanning-material is *tannin* or *tannic acid*, contained in oak-bark. It is a derivative of gallic acid, into which it is converted by boiling with dilute hydrochloric acid. Tannin is optically active, and seems to have a somewhat complicated molecular structure.

It is best obtained from gall-nuts—pathological excrescences on the leaves and branches of the oak, caused by an insect. Turkish gall-nuts are especially rich in tannin, yielding as much as 65 per cent.

> Tannin imparts its characteristic bitter taste to many beverages—to tea which has been too long infused, for instance. The addition of milk removes this bitter taste, because the tannin forms an insoluble compound with the proteïns present in the milk.

Tannin is a white (sometimes yellowish), amorphous powder, readily soluble in water, only slightly in alcohol, and insoluble in ether. It forms salts with two equivalents of the metals, and precipitates many alkaloids, such as strychnine and quinine, from their aqueous solutions (471).

A distinction is drawn between the different kinds of tanning-substances, which have properties analogous to those of tannin, but differ from it in composition. They are named after the plants in which they are found: *kino-tannin*, *catechu-tannin*, *moringa-tannin*, *coffee-tannin*, *oak-tannin*, *quinine-tannin*, and others are known.

> **390.** The tannins find application in *medicine* and in the *tanning of hides*.
>
> In making leather, the hide is saturated with the tannin, because without this treatment it cannot be employed in the manufacture of shoes and other articles, since it soon dries to a hard, horn-like substance, or in the moist condition becomes rotten. When saturated with tannin it remains pliant, and does not decompose.
>
> The skin of an animal consists of three layers, the epidermis, the cuticle, and the fatty layer. The cuticle being the part made into leather, the two other layers are removed by suspending the hides in running water, when the epidermis and fatty layer begin to decom-

pose, and are removed by means of a blunt knife. Alternate horizontal layers of the hides thus prepared and oak-bark or some other material containing tannin are placed in large troughs or vats, which are then filled with water. At the end of six or eight weeks the hides are taken out and placed in a second vat containing fresh bark of stronger quality. This is continued with increasingly concentrated tannin solutions until the hides are perfectly tanned, the process lasting as long as two or three years, according to the thickness of the hide. Whether a hide is thoroughly saturated or tanned can be judged from the appearance of its cross-section, or by treatment with dilute acetic acid: if this treatment makes it swell up internally, it shows that the conversion into leather is incomplete.

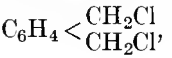
During the process of tanning, oxygen is taken up, indicating that the reaction involved is one of oxidation.

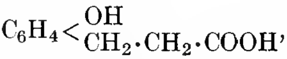
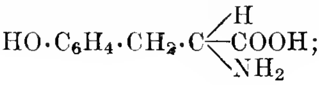
Acids Containing Hydroxyl or Carboxyl in the Side-chains.

391. Three different types of acids with hydroxyl or carboxyl in the side-chains are possible.

1. OH in the side-chain, COOH in the ring.
2. COOH in the side-chain, OH in the ring.
3. OH and COOH both in the side-chain.

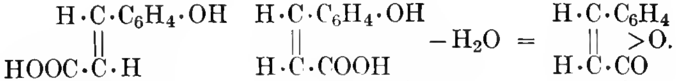
The following are representatives of these three classes.

1. *Hydroxymethylbenzoïc acid,*  $C_6H_4<\begin{matrix}CH_2OH & 1\\ COOH & 2\end{matrix}$, is mentioned in 368. It yields phthalide by separation of water, and is obtained by boiling o-*xylylene chloride,*  $C_6H_4<\begin{matrix}CH_2Cl\\ CH_2Cl\end{matrix}$, with water and lead nitrate.

2. p-*Hydroxyphenylpropionic acid,*  $C_6H_4<\begin{matrix}OH\\ CH_2\cdot CH_2\cdot COOH\end{matrix}$, is of some importance owing to its relation to *tyrosine* (M.P. 235°)—which derives its name from its presence in old cheese (Greek, *τυρόσ*), and is produced when proteïns, such as white of egg, horn, hair, etc., are boiled with hydrochloric acid or sulphuric acid. Its formula is $C_9H_{11}O_3N$, and its structure  $HO\cdot C_6H_4\cdot CH_2\cdot C\begin{matrix}H\\ COOH\\ NH_2\end{matrix}$; it is the

α-amino-acid of *p*-hydroxyphenylpropionic acid. Being an amino-acid, it yields salts with acids as well as with bases.

o-*Hydroxycinnamic acid*, $C_6H_4<\begin{matrix}OH\\ CH:CH\cdot COOH\end{matrix}$, exists in two forms, *coumaric acid* and *coumarinic acid*, which are easily converted into each other. Coumarinic acid is not known in the free state, but only in the form of salts, since, on liberation, it at once loses a molecule of water, yielding *coumarin*, the aromatic principle of woodruff (*Asperula odorata*). Coumaric acid, on the other hand, does not yield a corresponding anhydride: removal of water produces coumarin, which is converted into salts of coumarinic acid by treatment with alkalis. This behaviour recalls that of fumaric acid and maleïc acid (170), and it may be assumed that the stereoisomerism of these acids is similar. Both can then be represented as follows:



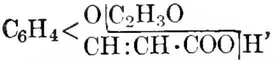
$$\begin{array}{c}\mathrm{H\cdot C\cdot C_6H_4\cdot OH}\\ \|\\ \mathrm{HOOC\cdot C\cdot H}\end{array} \qquad \begin{array}{c}\mathrm{H\cdot C\cdot C_6H_4\cdot OH}\\ \|\\ \mathrm{H\cdot C\cdot COOH}\end{array} - H_2O = \begin{array}{l}\mathrm{H\cdot C\cdot C_6H_4}\\ \ \ \| \quad >O.\\ \mathrm{H\cdot C\cdot CO}\end{array}$$

Coumaric acid; gives no corresponding anhydride

Coumarinic acid; only known in the form of salts

Coumarin

Coumarin can be obtained from salicylaldehyde by SIR WILLIAM PERKIN's synthesis (348): acetylcoumaric acid,



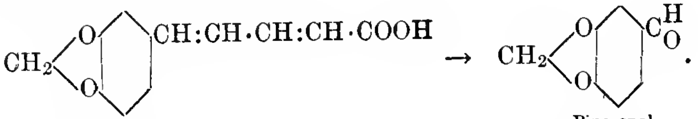
$$C_6H_4<\begin{matrix}O|\underline{C_2H_3O}\\ \overline{CH:CH\cdot COO}|H\end{matrix},$$

is first formed, and is converted into coumarin by heating, acetic acid being eliminated.

3. *Mandelic acid* has both hydroxyl and carboxyl in the side-chain. Its constitution is $C_6H_5\cdot CHOH\cdot COOH$, as its synthesis from benzaldehyde and hydrocyanic acid indicates. The mandelic acid found in nature is lævo-rotatory. The synthetical acid can be resolved by the action of cultures obtained from mildew (*Penicillium glaucum*), the dextro-rotatory acid being left intact. The decomposition is also effected by the formation of the cinchonine salts, when the salt of the dextro-rotatory acid crystallizes out first.

Inactive mandelic acid is also called "para-mandelic acid." It melts at 119°, and dissolves very readily in water: the optically active modification melts at 134°, and is less soluble in water.

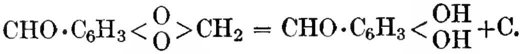
392. The unsaturated *piperic acid*, $C_{12}H_{10}O_4$, is a decomposition-product of piperine (**454**). Oxidation converts piperic acid into *piperonal*,



Piperic acid

Piperonal

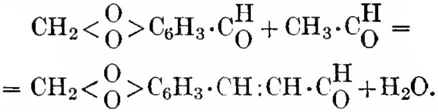
The constitution of this substance is established by two reactions. First, on heating with hydrochloric acid it is converted into *protocatechualdehyde* and carbon:



$$\mathrm{CHO\cdot C_6H_3<\substack{O\\O}>CH_2 = CHO\cdot C_6H_3<\substack{OH\\OH}+C.}$$

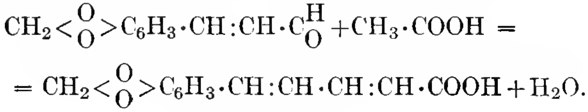
Second, it is regenerated by the action of methylene iodide and alkali upon this aldehyde.

Piperonal melts at 37°, and boils at 263°: its odour exactly resembles that of heliotropes. In presence of caustic soda, piperonal condenses with acetaldehyde to *piperonylacroleïn:*



$$\mathrm{CH_2<\substack{O\\O}>C_6H_3\cdot C\substack{H\\O} + CH_3\cdot C\substack{H\\O} =}$$
$$\mathrm{= CH_2<\substack{O\\O}>C_6H_3\cdot CH:CH\cdot C\substack{H\\O} + H_2O.}$$

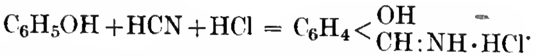
By PERKIN's synthesis (**348**), piperonylacroleïn is converted by the action of sodium acetate and acetic anhydride into piperic acid:



$$\mathrm{CH_2<\substack{O\\O}>C_6H_3\cdot CH:CH\cdot C\substack{H\\O} + CH_3\cdot COOH =}$$
$$\mathrm{= CH_2<\substack{O\\O}>C_6H_3\cdot CH:CH\cdot CH:CH\cdot COOH + H_2O.}$$

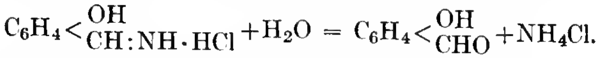
Hydroxyaldehydes.

393. *Hydroxyaldehydes* can be obtained artificially by a synthetical method generally applicable to the preparation of aromatic hydroxyaldehydes. It consists in treating the phenols in ethereal solution with anhydrous hydrocyanic acid and hydrochloric-acid gas, it being sometimes an advantage to add a small quantity of zinc chloride as a condensing agent. This mode of synthesis was discovered by GATTERMANN, whose name it bears. The hydrochloride of an imide is formed as an intermediate product, and can sometimes be isolated:



$$C_6H_5OH + HCN + HCl = C_6H_4<\begin{matrix}OH\\ CH:NH\cdot HCl\end{matrix}.$$

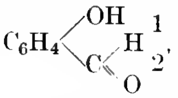
On treatment with warm water, the imide-salt is converted into the hydroxyaldehyde and ammonium chloride:



$$C_6H_4<\begin{matrix}OH\\ CH:NH\cdot HCl\end{matrix} + H_2O = C_6H_4<\begin{matrix}OH\\ CHO\end{matrix} + NH_4Cl.$$

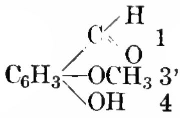
p-*Hydroxybenzaldehyde* is here obtained from phenol.

Salicylaldehyde, $C_6H_4\begin{cases}OH & 1\\ CHO & 2\end{cases}$, occurs in volatile *oil of spiræa.*



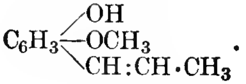
The *o*-hydroxyaldehydes colour the skin deep yellow.

To this class of substances belongs *vanillin,*



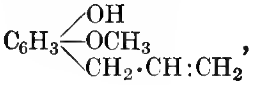
$$C_6H_3\begin{cases}CHO & 1\\ OCH_3 & 3'\\ OH & 4\end{cases}$$

the methyl ether of protocatechualdehyde. It is the aromatic principle of vanilla, and is prepared on the large scale by oxidizing *isoeugenol,*



$$C_6H_3\begin{cases}OH\\ OCH_3\\ CH:CH\cdot CH_3\end{cases}.$$

This substance is obtained by boiling *eugenol,*



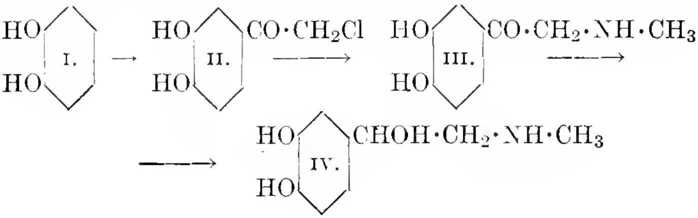
$$C_6H_3\begin{cases}OH\\ OCH_3\\ CH_2\cdot CH:CH_2\end{cases},$$

with alcoholic potash, which alters the position of the double linking in the side-chain. Eugenol is the chief constituent of oil of cloves.

Adrenaline, $C_9H_{13}ON$.

394. *Adrenaline* is prepared from the suprarenal capsules of the horse and other animals. It is characterized by its powerful hæmostatic properties. On oxidation, it yields protocatechuic acid, and on distillation with caustic soda, methylamine. With benzoyl chloride it forms a tribenzoyl derivative.

It is synthetically prepared by a German firm, the Farbwerke vormals Meister, Lucius und Brüning. Chloroacetyl chloride reacts with catechol (I.) to form *chloroacetylcatechol* (II.). On treatment with methylamine, this substance yields an amino-ketone (III.), reducible to adrenaline (IV.):



IV. COMPOUNDS WITH THE NITRO-GROUP AND AMINO-GROUP.

Nitroanilines.

395. *Nitroanilines* can be obtained by the partial reduction of dinitro-compounds by means of ammonium sulphide. Another method for their production consists in the nitration of anilines, though if nitric acid is allowed to act directly on this base the resulting products are mostly those of oxidation. If nitration is to be carried out, the amino-group must be "protected" against the action of this acid, either by first converting the aniline into acetoanilide, or by causing the nitric acid to react in presence of a large quantity of sulphuric acid. When the acetyl-compound is employed, p-*nitroaniline* is the chief product: with sulphuric acid, chiefly m-*nitroaniline* and *p*-nitroaniline are formed, and a very small proportion of the o-*nitroaniline*.

In these substances there is a weakening of the basic character, *m*-nitroaniline, for example, yielding salts which are decomposed by water.

o-Nitroaniline, *m*-nitroaniline, and *p*-nitroaniline, $C_6H_4 < \begin{matrix} NO_2 \\ NH_2 \end{matrix}$, are yellow, crystalline compounds, readily soluble in alcohol. Their melting-points are respectively 71°, 114°, and 147°.

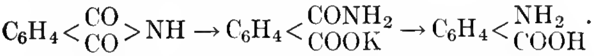
Nitrobenzoïc Acids.

396. m-*Nitrobenzoïc acid* is the principal product obtained by nitrating benzoïc acid; some o-*nitrobenzoïc acid* and a very small proportion of p-*nitrobenzoïc acid* are simultaneously formed. The *ortho*-compound is best obtained by the oxidation of *o*-nitrotoluene, and is characterized by an intensely sweet taste.

The introduction of the nitro-group causes a large increase in the value of the dissociation-constant 10^4k, which for benzoïc acid itself is 0·6, for *o*-nitrobenzoïc acid 61·6, for the *m*-acid 3·45, and for the *p*-acid 3·96. The melting-points of these acids are respectively 148°, 141°, and 241°.

Aminobenzoïc Acids.

397. The most important of the *aminobenzoïc acids* is o-*aminobenzoïc acid,* called *anthranilic acid,* first obtained by the oxidation of indigo (**468**). It has the character of an amino-acid, yielding salts with both acids and bases. It possesses a sweet taste and slightly antiseptic properties. It is obtained by the method of Hoogewerff and van Dorp (**264**), by treating phthalimide with bromine and caustic potash. The potassium salt of phthalaminic acid is first formed, and then changes into anthranilic acid:



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NH \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CONH_2}{COOK} \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{NH_2}{COOH}.$$

Phthalimide Potassium phthalaminate Anthranilic acid

Anthranilic acid melts at 145°, and can be sublimed without decomposition. It dissolves readily in water and in alcohol. By the method indicated it is prepared technically for the synthesis of indigo, bleaching-powder being substituted for the caustic potash and bromine. Its methyl ester causes the fragrance of many flowers. It has a powerful, but agreeable, odour, and finds application in the perfume-industry.

ORIENTATION OF AROMATIC COMPOUNDS.

398. *Orientation* is the determination of the relative positions occupied by the side-chains or substituents in the benzene-ring. A description of a number of the most important substitution-derivatives of benzene having been given in the foregoing pages, it becomes necessary to furnish an insight into the methods by which orientation is carried out.

These methods are based on two main principles.

1. *Relative determination of position.*—The compound with substituents in unknown positions is converted into another with known positions, it being inferred that the first compound has its substituents arranged similarly to the second. If, for example, the constitution of one of the three xylenes is required, the hydrocarbon can be oxidized. The particular phthalic acid formed indicates the positions of the methyl-groups in the xylene under examination, provided the positions of the carboxyl-groups in the three phthalic acids are known.

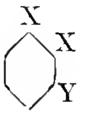
To apply this method, it is necessary to know the positions of the substituents in a small number of compounds, and it is further assumed that the positions of the substituents remain the same during the course of the reactions involved. Usually, this continuity holds, although the position of the side-chain does alter in a few reactions.

> The three bromo-sulphonic acids are converted into resorcinol by fusion with caustic potash (375). There are other examples of change of position when the sulpho-group is replaced by the hydroxyl-group, by fusion with caustic alkalis.

To avoid erroneous conclusions, it is, therefore, desirable in cases of doubt to check the determination of position by converting the substance into another compound.

2. *Absolute determination of position.*—The positions of the substituents are determined without the aid of other compounds with substituents in known positions. A general method is afforded by Körner's *principle*, by which it is possible to ascertain whether substances $C_6H_4X_2$, containing two substituents, are *ortho*-compounds, *meta*-compounds, or *para*-compounds, effected by determining the number of trisubstitution-products corresponding to them.

When a third group, Y, is introduced into an *ortho*-compound, $C_6H_4X_2$, whether Y is the same as or different from X, only two isomerides can be formed,



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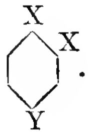
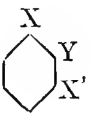
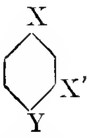


The introduction of a third group into a *meta*-compound renders possible the formation of three isomerides,





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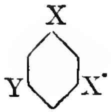
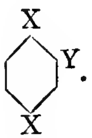


With a *para*-compound the introduction of a third group yields only one trisubstitution-product,

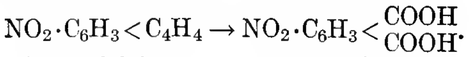


In addition to this general method, there are other special methods, several of which are described. They substantiate fully the conclusions already arrived at by Körner's method.

1. Absolute Determination of Position for *ortho*-Compounds.

399. For the *ortho*-series, the structure of a dibromobenzene melting at $-1°$ is determined by means of KÖRNER's principle: this body yields two isomeric nitrodibromobenzenes. The constitution of a *xylene* boiling at 142° and melting at $-28°$ has also been established by this method: it gives rise to two isomeric nitroxylenes when treated with nitric acid. This xylene is converted into phthalic acid by oxidation, proving that the latter is an *ortho*-compound.

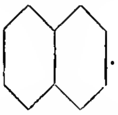
The oxidation of naphthalene (431), $C_{10}H_8$, to phthalic acid also proves that the carboxyl-groups of this acid are in the *ortho*-position. This reaction indicates that the structure of naphthalene must be $C_6H_4<C_4H_4$, the group C_4H_4 being linked to two positions in the benzene-ring. When naphthalene is treated with nitric acid, nitronaphthalene is formed, and is converted by oxidation into nitrophthalic acid. The group C_4H_4 has, therefore, been converted into two carboxyl-groups:



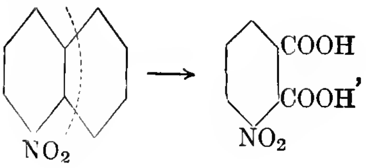
$$\underset{\text{Nitronaphthalene}}{NO_2\cdot C_6H_3<C_4H_4} \rightarrow \underset{\text{Nitrophthalic acid}}{NO_2\cdot C_6H_3<{}^{COOH}_{COOH}}.$$

Nitronaphthalene Nitrophthalic acid

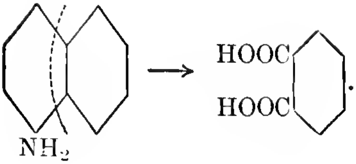
If, however, the nitro-group is reduced, and the aminonaphthalene thus obtained oxidized, phthalic acid is formed. Hence, the group C_4H_4 forms a second benzene-ring with the two carbon atoms of the benzene-ring, so that naphthalene must be represented by the formula



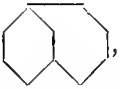
The oxidation of nitronaphthalene and aminonaphthalene is expressed by the scheme



and



Phthalic acid must, therefore, be an *ortho*-compound, because if it be assumed to have the *meta*-structure, for example, naphthalene must be represented by the formula

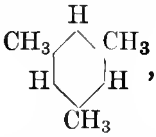


which involves a contradiction, for there could not then be a benzene derivative produced by the oxidation of *both* nitronaphthalene and aminonaphthalene.

2. Absolute Determination of Position for *meta*-Compounds.

400. The proof that mesitylene is symmetrical trimethylbenzene (1:3:5) is stated thus by Ladenburg.

If this compound has the constitution



the three hydrogen atoms directly linked to the benzene-ring must be of equal value. If this can be proved, the structure of mesitylene is established.

The proof of the equality is as follows. On nitrating mesitylene a dinitro-compound is obtained. If the hydrocarbon is represented by

$$\text{I.}\quad C_6(CH_3)_3\overset{a}{H}\overset{b}{H}\overset{c}{H},$$

the dinitro-compound may be arbitrarily assumed to be

$$\text{II.}\quad C_6(CH_3)_3\overset{a}{NO_2}\overset{b}{NO_2}\overset{c}{H}.$$

One of the nitro-groups of the dinitro-compound is reduced, and the resulting amino-compound is converted into an acetyl-derivative: suppose that this acetyl-derivative is

$$\text{III.}\quad C_6(CH_3)_3\overset{a}{N}O_2NH(\overset{b}{C}_2H_3O)\overset{c}{H}.$$

This substance can be again nitrated, when there must result

$$C_6(CH_3)_3\overset{a}{N}O_2NH(\overset{b}{C}_2H_3O)\overset{c}{N}O_2.$$

It is possible to eliminate the acetylamino-group, $NH(C_2H_3O)$, from this compound by saponification, subsequent diazotization, etc. A dinitromesitylene with the formula

$$C_6(CH_3)_3\overset{a}{N}O_2\overset{b}{H}\overset{c}{N}O_2$$

is obtained, identical with the former dinitro-product, the nitro-groups of which are at *a* and *b*. It follows that

$$H^b = H^c.$$

Nitromesidine, $a:b$, the acetyl-compound of which is represented by formula III., furnishes a further proof that $H^a = H^c$. When the amino-group is eliminated by means of the diazo-reaction, there is formed

$$\text{IV.}\quad C_6(CH_3)_3\overset{a}{N}O_2\overset{b}{H}\overset{c}{H}.$$

This substance is reduced, and converted into an acetyl-compound, acetylmesidine,

$$C_6(CH_3)_3NH(\overset{a}{C}_2H_3O)\overset{b}{H}\overset{c}{H},$$

which can be again nitrated, yielding

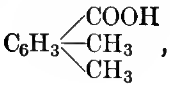
$$C_6(CH_3)_3NH(\overset{a}{C}_2H_3O)\overset{b}{N}O_2\overset{c}{H}.$$

It is immaterial whether the nitro-group of this compound is at *b* or *c*, since the equality of these positions relative to *a* has been already proved.

On eliminating the acetylamino-group from the last substance, a mononitromesitylene is produced, identical with the compound IV. Hence, $a = b = c$, which completes the proof of the equality of the three hydrogen atoms.

From the known constitution of mesitylene it is possible to deduce the structure of many other compounds. For example,

partial oxidation converts it into *mesitylenic acid,*



$$C_6H_3\begin{cases}COOH\\CH_3\\CH_3\end{cases},$$

which is in turn converted into xylene by distillation with lime: this xylene must be the *meta*-compound. Oxidation converts *m*-xylene into *iso*phthalic acid, indicating that the carboxyl-groups in the latter occupy the *meta*-position. These determinations of position have been fully substantiated by the application of Körner's principle. Thus, Nölting has prepared three isomeric nitroxylenes, in which the relative positions of the methyl-groups are the same as in the xylene obtained from mesitylenic acid.

Among other *meta*-compounds in which the position of the groups has been independently established, is a dibromobenzene boiling at 220°. Körner proved that corresponding to this substance are three isomeric tribromobenzenes and three nitrodibromobenzenes. In conclusion, the phenylenediamine melting at 62° can be obtained from three different diaminobenzoïc acids by elimination of CO_2, so that it also must be a *meta*-compound.

3. Absolute Determination of Position for *para*-Compounds.

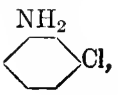
401. Körner's principle has been of great service in determining the constitution of some members of the *para*-series. For example, from the xylene boiling at 138°, and melting at 13°, it is only possible to obtain one nitroxylene: the phenylenediamine melting at 140° can only be obtained from one diaminobenzoïc acid by removing CO_2: and so on.

These determinations of position have been confirmed by another method, exemplified by the identification of a hydroxybenzoïc acid melting at 210° as a *para*-compound. The starting-point of the proof is bromobenzoïc acid, obtained directly by the bromination of benzoïc acid. On nitration, two isomeric nitrobromobenzoïc acids are formed, either of which yields on reduction the same aminobenzoïc acid, anthranilic acid. This acid can be converted into salicylic acid by means of the diazo-reaction. It follows that in both the isomerides the nitro-group must be situated symmetrically to the carboxyl-group; at 2 or 6, or at 3 or 5, if the carboxyl-group is at 1. The same reasoning establishes the position of the hydroxyl-group in salicylic acid. The bromine atom cannot be at 4, because two isomeric nitro-compounds which would yield the same aminobenzoïc acid on reduction could not be obtained from

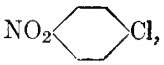
The bromine atom must, therefore, occupy the *meta*-position or *ortho*-position to the carboxyl-group. A hydroxybenzoïc acid melting at 200°, corresponding with this acid must be, therefore, *meta* or *ortho*. Since the isomeric salicylic acid can also be only a *meta*-compound or an *ortho*-compound, there remains no possibility, except the *para*-structure, for the third hydroxybenzoïc acid melting at 210°.

Determination of Position for the Trisubstituted and Higher-substituted Derivatives.

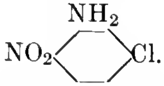
402. This orientation can usually be effected by ascertaining the relation in which they stand to the di-derivatives of known constitution. For example, since a certain chloronitroaniline, $C_6H_3Cl(NO_2)(NH_2)$, is obtained by nitrating *m*-chloroaniline,



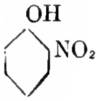
and yields *p*-chloronitrobenzene,



by exchange of the amino-group for hydrogen, it must have the constitutional formula

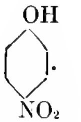


403. A more complicated example of orientation is afforded by the determination of the positions of the groups in *picric acid.* Careful nitration converts phenol into two mononitrophenls,



M.P. 45°

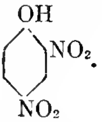
and



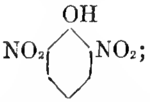
M.P. 114°

One of these mononitrophenols must be the *ortho*-compound and the other the *para*-compound, because the third nitrophenol can be obtained from *m*-dinitrobenzene—the constitution of which has been proved by its reduction to *m*-phenylenediamine (360)—by reduction to *meta*-nitroaniline, and subsequent exchange of NH_2 for OH by diazotizing.

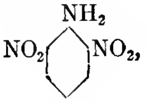
When further nitrated, both nitrophenols yield the same dinitrophenol, which can therefore only have the formula



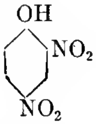
The mononitrophenol melting at 114° is converted by oxidation into benzoquinone (356), and must, therefore, be the *para*-compound. For the body melting at 45° there remains only the *ortho*-structure. On nitration this *o*-nitrophenol yields, in addition to the 1:2:4-dinitrophenol (OH at 1), another dinitrophenol with its groups at 1:2:6,



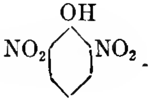
for on conversion of this into its methyl ether, and heating the latter with alcoholic ammonia, the group OCH_3 is replaced by NH_2; and this substance, which has the formula



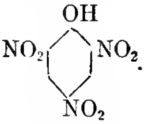
is converted by substitution of hydrogen for the NH_2-group into the ordinary *meta*-dinitrobenzene. Thus, we have two dinitrophenols of known structure,



and



Further nitration converts both into picric acid, which must, therefore, have the constitution



From the constitution of picric acid may be inferred the position of the groups in ordinary trinitrobenzene, since this compound is readily oxidized to picric acid (359). This trinitrobenzene must, accordingly, have the symmetrical structure.

Equivalence of the Six Hydrogen Atoms in Benzene.

404. It is stated in 288 that benzene does not yield isomeric mono-substitution-products, and the inference is drawn that the six hydrogen atoms of this hydrocarbon are of equal value.

There are several direct methods of proving this equivalence, one of them, devised by Nölting, being characterized by its simplicity. If the six hydrogen atoms are denoted by *a*, *b*, *c*, *d*, *e*, and *f*, the amino-group in aniline may be arbitrarily assumed to be at *a*. When bromobenzene, obtained from aniline by the diazo-reaction (341, 4), is treated with methyl iodide, and sodium it yields toluene. On nitration, three isomeric nitrotoluenes are obtained—the proportion of the *meta*-compound being very small. In these compounds the CH_3 group is at *a*, so that the nitro-groups may be arbitrarily assumed to be at *b*, *c*, and *d* respectively. On reduction, the three corresponding toluidines result:

$C_6H_5{\cdot}CH_3\ (a) \rightarrow CH_3{\cdot}C_6H_4{\cdot}NO_2\ (b{:}c{:}d) \rightarrow COOH{\cdot}C_6H_4{\cdot}NH_2\ (b{:}c{:}d)$.

After protection of the amino-group in each of these compounds by acetylation, the three aminobenzoïc acids are obtained by oxidation. These acids yield, by elimination of CO_2,the same aniline, identical with the original substance. It follows that $a=b=c=d$.

The starting-point of the proof of the equivalence of e and f to a, b, c, and d is *o*-toluidine, in which the CH_3-group may be assumed to be at a, and the NH_2-group at b. Nitration of its acetyl-derivative, followed by elimination of the acetyl-group, produces simultaneously four nitro-*o*-toluidines. Since a and b are occupied, the nitro-groups must be at c, d, e, and f respectively. Replacement of the amino-group by hydrogen yields four nitrotoluenes, $a{:}c$, $a{:}d$, $a{:}e$, and $a{:}f$. The first two are *m*-nitrotoluene and *p*-nitrotoluene: they are also obtained by direct nitration of toluene, as described in the previous paragraph. The nitrotoluene $a{:}e$ is identical with $a{:}c$, and $a{:}f$ with $a{:}b$, which indicates the equivalence of c to e and of b to f, thus completing the proof.

Influence of the Substituents on Each Other.

405. The influence of the substituents on each other is very important, and manifests itself in various ways. It affects the relative positions taken up by the substituents, when introduced simultaneously or in succession into the benzene-nucleus. Let the simplest case be considered first, the introduction of a second atom or group into a monosubstituted compound C_6H_5X. One of the three possible isomerides is always obtained as the chief product the second isomeride being produced in less quantity, while the yield of the third isomeride is very small. For example, when benzoïc acid is nitrated at 0°, 80·2 per cent. of *m*-nitrobenzoïc acid, 18·5 per cent. of *o*-nitrobenzoïc acid, and only 1·3 per cent. of *para*-nitrobenzoïc acid are formed. On nitration at 30°, nitrobenzene yields 90·9 per cent. of *m*-dinitrobenzene, 8·1 per cent. of *o*-dinitrobenzene, and 1 per cent. of *p*-dinitrobenzene. It has often been stated that the introduction of a second group results in the formation of only one or two isomerides; but when a careful examination has been made as to the presence of the third isomeride, it has been shown to be present in minute quantity; so that it is probable that the three isomerides are always formed, although in very different proportions.

The relative proportions of the different isomerides formed depend upon three factors: the particular substituent already in the nucleus; the group introduced; and the temperature of substitution. It is also influenced by certain other conditions. The table indicates how these quantities depend upon the two first-mentioned factors, the numbers in brackets indicating the by-products.

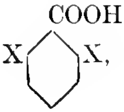
Element or Group already present (in Position 1).	Position entered by Substituents.				
	Cl	Br	I	SO_3H	NO_2
Cl	4(2)	4(2)	4	4	4(2)
Br		4(2)		4	4(2)
I					4(2)
OH	4(2)	4(2)	4 (2)	4(2)	4(2)
SO_3H		3		3(4)	3(2)(4
NO_2	3			3(2)(4)	3(2)(4)
NH_2	4	4	4	4	4(2)
CH_3	4(2)	4(2)		4(2)	4(2)
COOH	3	3	3	3(4)	3(2)(4)
CN		4			3

It is apparent that there is an opposition between the formation of *ortho*-derivatives and *para*-derivatives on the one hand, and of *meta*-derivatives on the other. Either the two first are the chief products, or the last. Concerning the influence of temperature, it has been proved by researches on nitration that the quantity of the by-products is the smaller, the lower the temperature of nitration.

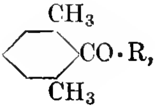
This opposition between *ortho*-derivatives and *para*-derivatives on the one hand, and *meta*-derivatives on the other, is not only observed in their preparation, but also in many of their properties. As a class, the *meta*-compounds are more stable towards reagents than the *ortho*-derivatives and *para*-derivatives. An example is given in 359. It may be further noted that *o*-nitrobromobenzene and *p*-nitrobromobenzene, $C_6H_4BrNO_2$, are converted by ammonia into the corresponding nitroanilines, $C_6H_4(NH_2)NO_2$, whereas *m*-bromonitrobenzene does not react with ammonia.

406. *Ortho*-groups sometimes exert a remarkable influence in retarding or partially preventing reactions which take place readily in their absence. The following reactions exemplify this phenomenon.

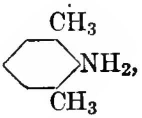
When an acid is dissolved in excess of absolute alcohol it can be almost quantitatively converted into an ester by passing a current of hydrochloric-acid gas through the mixture (99). Victor Meyer and his students found, however, that esterification of acids containing two groups in the *ortho*-position relative to carboxyl,



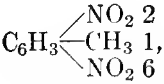
could not be thus effected. On the other hand, when the acid has been converted into an ester (by means of the silver salt and an alkyl halide) the ester so formed can only be saponified with difficulty. When the two substituents occupy any of the other positions, these peculiarities do not manifest themselves, or at least not to the same extent. Ketones substituted in the two *ortho*-positions,



where R is an alkyl-radical, cannot be converted into oximes, wherein they differ from all other ketones. *o*-*o*-Dimethylaniline,

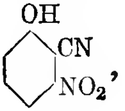


is not converted by treatment with an alkyl iodide into a quaternary base. Pentamethylbenzonitrile, $C_6(CH_3)_5CN$, cannot be hydrolyzed to the corresponding acid. The methyl-hydrogen in *o*-*o*-dinitrotoluene,

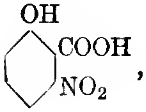


$$C_6H_3\begin{cases} NO_2 & 2 \\ CH_3 & 1, \\ NO_2 & 6 \end{cases}$$

cannot be replaced by halogens even at a high temperature (200°), as is also true of 1:2:4-dinitrotoluene. In spite of numerous attempts, the hydrolysis of *o*-nitrosalicylonitrile,

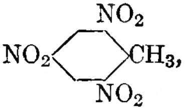


to the corresponding acid,



has not been effected.

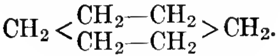
Groups occupying positions further separated sometimes exert a similar effect. One of the NO_2-groups of symmetrical trinitrobenzene is replaced by OCH_3 through the action of sodium methoxide: for trinitrotoluene,



this substitution is not found possible, the methyl-group preventing exchange of the nitro-group even in the *para*-position.

HYDROCYCLIC OR HYDROAROMATIC COMPOUNDS.

407. A number of compounds occur in nature containing proportions of hydrogen intermediate between those in the aromatic derivatives with saturated side-chains and those in the saturated aliphatic derivatives. These *hydrocyclic* or *hydroaromatic* compounds are readily converted into aromatic bodies. Caucasian petroleum contains *naphthenes*, with the formula C_nH_{2n}, which have two hydrogen atoms less than the corresponding saturated hydrocarbons, C_nH_{2n+2}, but nevertheless display all the properties characteristic of saturated compounds. The explanation is that they lack multiple bonds, but have a closed carbon chain; thus,



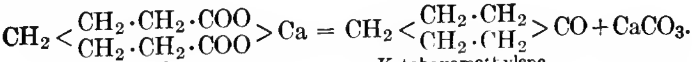
$$CH_2 < \begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix} > CH_2.$$

Hexamethylene

The *terpenes*, $C_{10}H_{16}$, are vegetable-products, and are the principal constituents of the "essential oils." These oils also contain compounds of the formulæ $C_{10}H_{16}O$, $C_{10}H_{18}O$, and $C_{10}H_{20}O$, among them the *camphors*. Like the naphthenes, the terpenes and camphors are readily converted into aromatic compounds, and therefore belong to the hydrocyclic series. The progress recently made in this division of organic chemistry has rendered a systematic classification of these compounds possible.

408. Two principal methods are employed in their preparation: by one they are got from compounds of the aliphatic series, and by the other from those of the aromatic series. Several examples of each method will be cited.

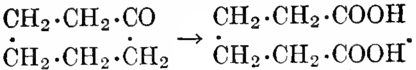
On dry distillation, calcium adipate yields ketopentamethylene (**284**). By the same treatment calcium pimelate is converted into *ketohexamethylene:*



$$CH_2 < \begin{matrix} CH_2\cdot CH_2\cdot COO \\ CH_2\cdot CH_2\cdot COO \end{matrix} > Ca = CH_2 < \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} > CO + CaCO_3.$$

Calcium pimelate — Ketohexamethylene

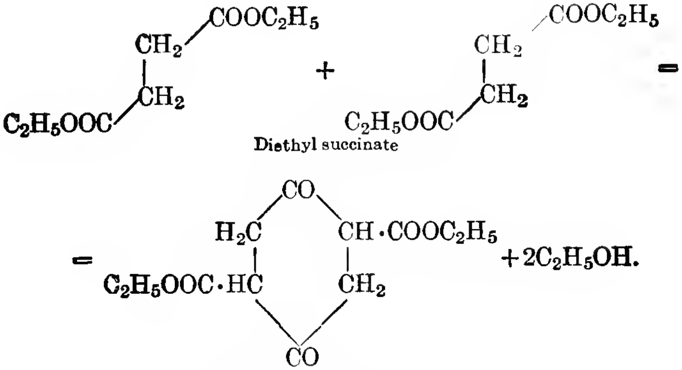
This structural formula is established by the ketonic character of the compound, and by the fact that dilute nitric acid oxidizes it almost quantitatively to adipic acid:



$$\begin{matrix} \mathrm{CH_2\cdot CH_2\cdot CO} \\ \mathrm{CH_2\cdot CH_2\cdot CH_2} \end{matrix} \rightarrow \begin{matrix} \mathrm{CH_2\cdot CH_2\cdot COOH} \\ \mathrm{CH_2\cdot CH_2\cdot COOH} \end{matrix}.$$

Ketohexamethylene Adipic acid

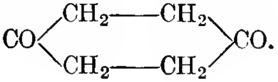
Diethyl succinate constitutes an important basis for the synthesis of other hexamethylene derivatives. In presence of sodium, two molecules of it condense to diethyl succinylsuccinate, which melts at 127°:



Diethyl succinate

Diethyl succinylsuccinate

The free acid, obtained by saponification, is decomposed at 200°, with elimination of two molecules of carbon dioxide, yielding p-*diketohexamethylene*,



The structural formula of this substance is indicated by this synthesis, and also by its reduction to ketohexamethylene.

409. The second method of obtaining hydrocyclic compounds has been much simplified by the researches of Sabatier and Senderens. They found that many aromatic hydrocarbons, such as benzene and its homologues, are readily hydrogenated to hexamethylene and its derivatives by passing their vapours mixed with hydrogen over

heated, finely-divided nickel, which is obtained by reduction of the oxide, and exerts a catalytic influence:

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 = \underset{\text{Hexamethylene}}{C_6H_{12}}.$$

Benzoïc acid can be hydrogenated to *hexahydrobenzoïc acid* by the action of sodium on its solution in amyl alcohol at the boiling-point. The phthalic acids and polybasic aromatic acids are hydrogenated by treating them in aqueous solution with sodium-amalgam.

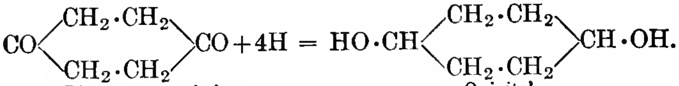
In describing the hydrocyclic compounds, it is convenient to treat the cymene derivatives, or terpenes, separately, for they exhibit many characteristic properties. The other hydrocyclic compounds will first be briefly reviewed.

410. *Hexamethylene* is the simplest member of this group. It is best obtained by the method of SABATIER and SENDERENS (409). Like its homologues, it is a colourless liquid. Its boiling-point, 80°, is very near that of benzene, 80·4°: as the crude hydrogenation-product always contains benzene, the isolation of pure hexamethylene from it by fractional distillation is therefore impracticable. In its separation, advantage is taken of its stability at ordinary temperatures towards fuming sulphuric acid and concentrated nitric acid, which respectively convert benzene into benzenesulphonic acid and nitrobenzene. Since each of these compounds is soluble in the corresponding acid, and hexamethylene insoluble, the separation of the latter can be readily effected. The melting-point (89) affords the best criterion of the purity of hexamethylene. It is 6·4°, and therefore approximates closely to that of benzene, 5·4°.

Chlorine reacts very energetically with hexamethylene in diffused sunlight, and with explosive violence in direct sunlight. A mixture of substitution-products is formed, from which *monochlorohexamethylene* can be obtained by fractional distillation. Replacement of the Cl-atom in this compound by hydroxyl is not readily effected: treatment with alcoholic potash converts it into *tetrahydrobenzene*, a liquid boiling at 83°–84°, and possessing all the properties characteristic of unsaturated compounds.

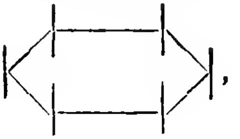
When a mixture of phenol-vapour and hydrogen is passed over finely-divided nickel, *hexahydrophenol* is formed. It is a colourless, somewhat thick liquid: it boils at 160·5°, and at a low temperature solidifies to a camphor-like mass, which melts at 20°.

p-Diketohexamethylene (408) melts at 78°. Careful reduction with sodium-amalgam in an atmosphere of carbon dioxide converts it into the dihydric alcohol *quinitol:*

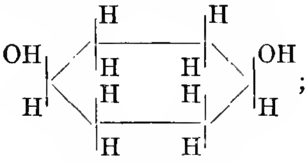


p-Diketohexamethylene Quinitol

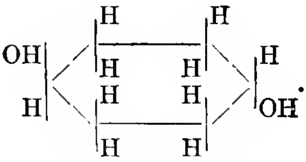
Two modifications of quinitol are known, distinguished by the prefixes *cis* and *trans*. They are best prepared from quinol by the reduction-method of SABATIER and SENDERENS (409). They can be separated by means of their acetyl-derivatives. The stereochemical character of their isomerism is indicated by a consideration of Fig. 33 (169), in which a pentamethylene-ring is represented. If the pentagon is supposed to lie in the plane of the paper, one of the free linkings of each carbon atom will lie above, and the other below, this plane. If a hexamethylene-ring is similarly constructed, there is obtained the perspective figure



in which the affinities not forming part of the ring are represented by vertical lines. The isomerism of the quinitols is explained by the assumption that the hydroxyl-groups of the *cis*-modification are situated on the same, and of the *trans*-modification on the opposite, side of the hexagon:



cis-Quinitol (M. P. 101°)

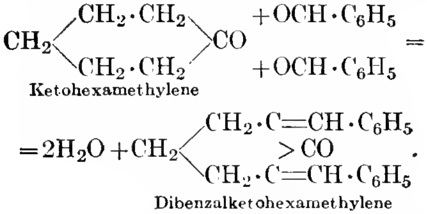


trans-Quinitol (M. P. 139°)

411. *Inositol*, $C_6H_{12}O_6$, is a hexahydric alcohol derived from hexamethylene. Its molecular formula is the same as that of the hexoses: on account of its sweet taste and its occurrence in many leguminous plants, it was formerly classed with the sugars. Its relation to hexamethylene is proved by its reduction with hydriodic acid to

benzene, phenol, and tri-iodophenol, and by its conversion by phosphorus pentachloride into quinone and substituted quinones. The presence of six hydroxyl-groups is indicated by the formation of a hexa-acetate. Inositol is also a constituent of the heart-muscle, the liver, and the brain.

Ketohexamethylene can be prepared from pimelic acid (408), but is more readily obtained by the oxidation of hexahydrophenol with chromic acid. It boils at 155°. Its alkaline solution reacts with benzaldehyde to form a well-crystallized condensation-product:



$$CH_2\left\langle\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right\rangle CO \quad \begin{matrix}+OCH\cdot C_6H_5\\ +OCH\cdot C_6H_5\end{matrix} =$$

$$=2H_2O+CH_2\left\langle\begin{matrix}CH_2\cdot C{=}CH\cdot C_6H_5\\ >CO\\ CH_2\cdot C{=}CH\cdot C_6H_5\end{matrix}\right. .$$

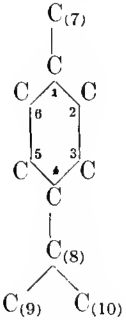
This reaction furnishes a good test for ketohexamethylene.

The properties of the hydrocyclic acids are analogous to those of the aliphatic acids. Thus, *hexahydrobenzoïc acid* has a rancid odour, like that of capric acid. It melts at 92°, almost 30° lower than benzoïc acid, which melts at 121·4° The hydrophthalic acids exhibit isomerism which admits of the same explanation as that of quinitol.

TERPENES.

412. The *terpenes* are hydrogenated derivatives of cymene and its substitution-products. Many of them are vegetable products. They are readily volatile with steam, and this property facilitates the isolation of the natural terpenes. The distillate separates into two parts, an aqueous layer below, and a mixture of terpenes above. After drying, the terpene-layer is fractionated several times *in vacuo* to isolate its constituents. Complete purification has sometimes to be effected by conversion of the terpenes into derivatives which can be freed from impurities by crystallization: from the crystalline compounds thus obtained the terpenes can be regenerated.

Von Baeyer has devised a rational nomenclature for the numerous derivatives of hydrogenated cymene. He numbers the carbon atoms of this hydrocarbon as in the scheme

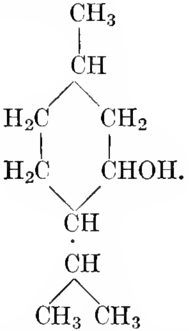


A double linking between two carbon atoms, such as 3 and 4, is denoted by Δ^3.

The saturated cyclic hydrocarbon *hexahydrocymene*, $C_{10}H_{20}$, is called *menthane*. It is not a natural product, but can be obtained by the interaction of cymene and hydrogen with nickel as a catalyst. It boils at 170°.

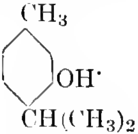
The saturated alcohols and ketones derivable from menthane are very important. Among them is *menthol* or 3-*menthanol*, $C_{10}H_{20}O$, the principal constituent of oil of peppermint, from which it crystallizes on cooling. It forms colourless prisms of characteristic peppermint-like odour. It melts at 43°.

Menthol has the constitution



Menthol

It is a secondary alcohol, since oxidation with chromic acid eliminates two atoms of hydrogen, yielding a substance of ketonic character, called *menthone*, a constituent of oil of peppermint. Since there are several processes for the conversion of menthol into cymene or its derivatives, it must contain a cymene-residue. One of these methods also proves that the hydroxyl-group is attached to carbon atom 3: when a solution of menthone in chloroform is treated with bromine, there results a *dibromomenthone*, from which quinoline eliminates 2HBr, forming thymol (**304**),

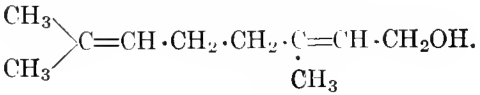


Thymol

When thymol is heated with phosphoric oxide, it yields propylene and *m*-cresol (**304**), so that its methyl-group and hydroxyl-group must be in the *meta*-position.

413. *Terpin*, $C_{10}H_{18}(OH)_2$, a dihydric alcohol, is also a derivative of menthane. Its *hydrate*, $C_{10}H_{20}O_2+H_2O$, is obtained by keeping oil of turpentine in contact with dilute nitric acid and a small proportion of alcohol in shallow dishes for several days. During the process the turpentine takes up the elements of three molecules of water. Terpin hydrate forms well-defined crystals, melting at 117°. On heating, it loses one molecule of water, anhydrous terpin distilling at 258°.

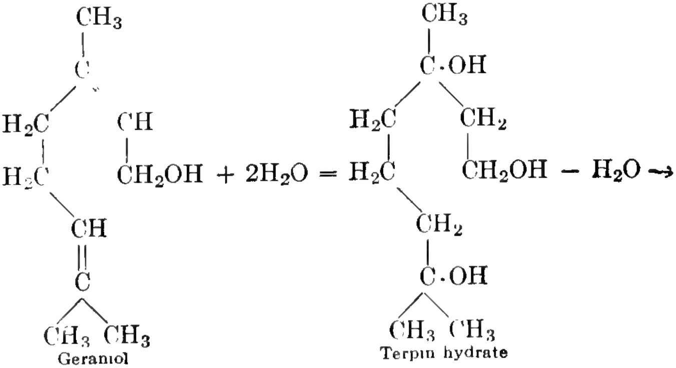
Terpin can be synthesized from geraniol,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH\cdot CH_2\cdot CH_2\cdot \underset{CH_3}{C}{=}CH\cdot CH_2OH.$$

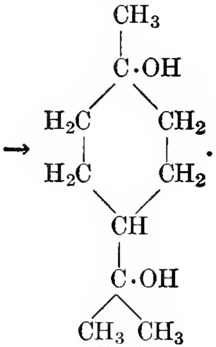
Geraniol

When agitated for a prolonged time with sulphuric acid of five per cent. strength, geraniol takes up two molecules of water, being almost quantitatively converted into terpin hydrate:



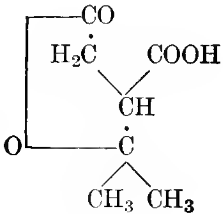
Geraniol

Terpin hydrate



Terpin

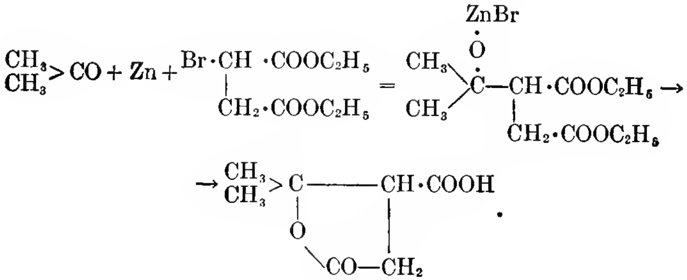
This mode of synthesis indicates that terpin is 1:8-dihydroxymenthane, and there is other evidence in favour of this view. Hydriodic acid reduces it to menthane, proving the presence of a cymene-nucleus. One of the hydroxyl-groups is at position 8, for when terpin is oxidized with nitric acid, *terebic acid,*



Terebic acid

is formed.

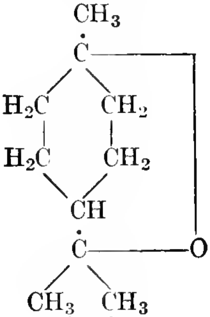
The constitution of terebic acid is established by its synthesis from diethyl bromosuccinate and acetone in presence of zinc:



Terebic acid

The synthesis of terpin from geraniol indicates that the second hydroxyl-group may be at 1 or at 2. If it is at 2, this carbon atom must be asymmetric; but terpin is optically inactive, and has not been resolved into optically active components. It therefore does not contain an asymmetric carbon atom, so that the second hydroxyl-group must be at position 1.

Elimination of water from terpin yields, among other products (**414**), a substance of the formula $C_{10}H_{18}O$, which is neither an alcohol nor a ketone, and is identical with *cineol*, a constituent of many essential oils. Oil of eucalyptus and oil of wormseed (*Oleum cinæ*) contain a large proportion of this compound. Its mode of formation and properties indicate that cineol has the constitutional formula

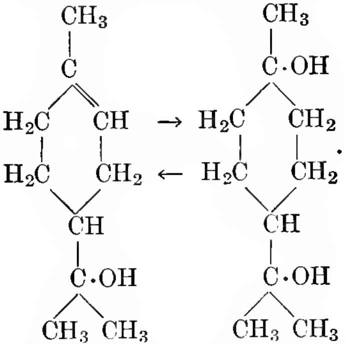


Cineol

414. Some of the unsaturated derivatives of menthane are also very important. The *menthenes*, $C_{10}H_{18}$, hydrocarbons with one double linking in their molecule, need not be considered, but the alcohol *terpineol* and the ketone *pulegone*, derived from them, merit description.

Terpineol, $C_{10}H_{18}O$, is a constituent of some essential oils. It has an odour resembling that of lilacs: it melts at 35°, and boils at 218°. Terpineol is closely related to terpin, since agitation with dilute sulphuric acid converts it into terpin hydrate: inversely, boiling with dilute sulphuric acid regenerates terpineol from terpin hydrate, with elimination of water.

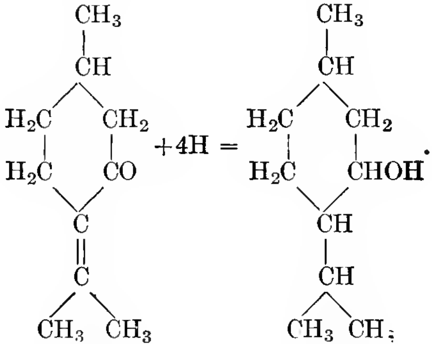
The constitution of terpineol must therefore be very similar to that of terpin, the only question being which of the hydroxyl-groups of the latter has been eliminated from the molecule along with one hydrogen atom. Since an optically active terpineol is known, it must be hydroxyl-group 1 of terpin, so that terpineol has the constitution indicated in the scheme



Terpineol Terpin

Carbon atom 4 in the formula given is asymmetric, whereas removal of water from C-atoms 4:8, 8:9 (=8:10), or 1:7 could not produce an asymmetric carbon atom.

Pulegone, $C_{10}H_{16}O$, is the principal constituent of the cheap oil of polei. It boils at 222°, and has a peppermint-like odour. The formation of an oxime indicates that it is a ketone. On reduction with sodium and alcohol, it takes up four hydrogen atoms, yielding menthol, which proves that the carbonyl-group is at position 3:

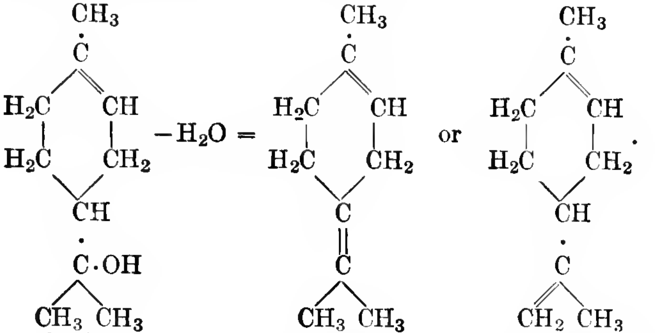


Pulegone Menthol

Both oxidation and heating with water decompose pulegone with formation of acetone, so that the double linking is between C-atoms 4 and 8.

415. Among the unsaturated menthane derivatives with two double linkings are the hydrocarbons *terpinolene*, d-*limonene*, and l-*limonene*, and their racemic form, *dipentene*. Each has the formula $C_{10}H_{16}$.

Terpinolene boils at 185°. It is formed when terpineol is boiled with oxalic-acid solution, one molecule of water being eliminated. Theoretically, two reactions are possible:



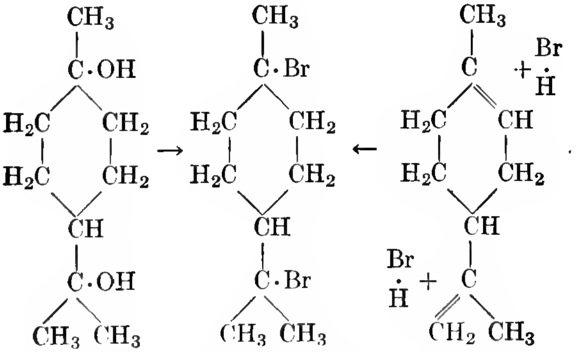
Terpineol I.

Terpinolene II.

d- and *l*- Limonene III.

Since terpinolene is optically inactive, and is derived from the optically active terpineol, the asymmetry of the carbon atom must have vanished, as in formula II. C-atom 4 of formula III. is asymmetric, as in terpineol itself, formula I.

Formula III. is that of the optically active limonene, which occurs in many essential oils and varieties of turpentine. It has an agreeable, lemon-like odour. Its constitution is inferred from two facts: first, it is also obtained from terpineol by elimination of water, effected by heating with potassium hydrogen sulphate; second, addition of 2HBr yields the same dibromomenthane as is obtained from terpin by exchange of the hydroxyl-groups for bromine:



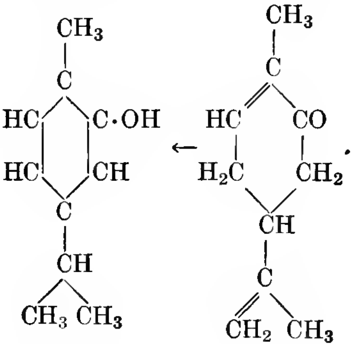
Terpin

Dibromomenthane

Limonene

Dipentene, a constituent of oil of turpentine, is also obtained by mixing *d*-limonene and *l*-limonene in equal proportions by weight. Like the limonenes, it yields a well-crystallized tetrabromide, indicating the presence of two double linkings in its molecule.

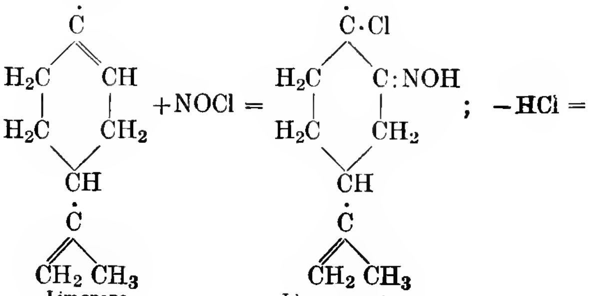
416. *Carvone*, $C_{10}H_{14}O$, is an important ketone belonging to this group. It is the principal constituent of oil of carraway, and has its characteristic odour. It boils at 228° Related to carvone is *carvacrol*, which is obtained from it by heating with caustic potash:



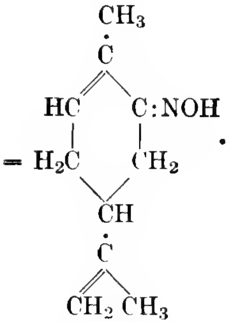
Carvacrol Carvone

The hydroxyl-group in carvacrol is linked to C-atom 2, since, on heating with phosphoric oxide, propylene is evolved, and *o*-cresol (304) formed. The carbonyl-group in carvone is assumed, therefore, to be at position 2. Carvone is proved to be a ketone by the formation of an oxime, called *carvoxime*.

When nitrosyl chloride is added to limonene, subsequent elimination of HCl yields carvoxime:



Limonene Limonene nitroso-chloride

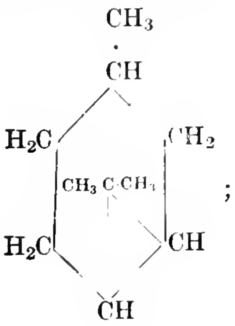


Carvoxime

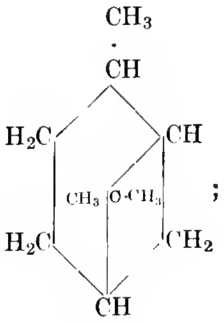
This reaction proves that carvone contains one double linking $\Delta^{8:9}$, but leaves it doubtful whether the other double linking is Δ^{6} or $\Delta^{1:7}$. In the production of terpineol from terpin the double linking is formed between two C-atoms of the nucleus, and by analogy this should also hold for carvone. Further evidence in favour of the formula indicated is afforded by the decomposition-products of the carvone molecule, but the details are beyond the scope of this work.

Polycyclic Terpene Derivatives.

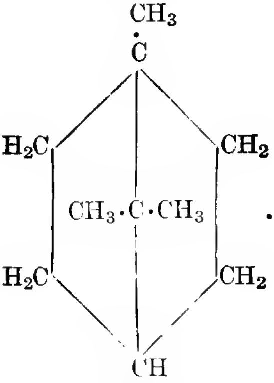
417. There exist hydrocarbons of the formula $C_{10}H_{16}$ which contain but one double linking, for they take up only two univalent atoms or groups. As they contain four hydrogen atoms less than the saturated cyclic menthane, $C_{10}H_{20}$, they must have a second closed chain in the molecule. Moreover, these compounds and their derivatives are closely related to cymene, most of them being convertible into it or kindred substances. Investigation has shown that the formation of the second ring can take place in three different ways, as the formulæ indicate:



Carane



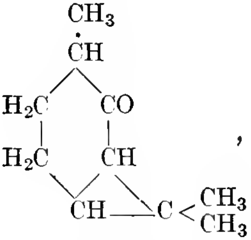
Pinane



Camphane

The tertiary carbon atom takes part in the formation of the ring, or "bridge-formation." *Carane* has a trimethylene-ring, *pinane* a tetramethylene-ring, and *camphane* a pentamethylene-ring. Several members of these three groups will be considered.

Carane itself is unknown, but there is a synthetic derivative, *carone*, which is not a natural product. It has the structural formula

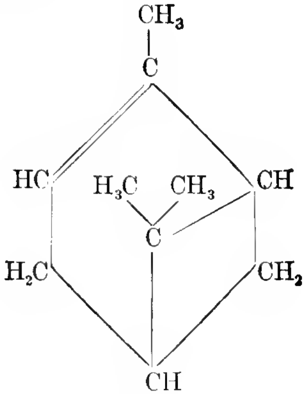


Carone

for opening of the trimethylene-ring at 3:8 yields derivatives of *p*-cymene, and at 4:8 derivatives of *m*-cymene.

Pinene is the typical member of the pinane-group. It is the principal constituent of the various oils of turpentine, and is, therefore, also of technical importance. It is optically active, a dextro-rotatory, a lævo-rotatory, and an inactive modification being known. It boils at 156°. The presence of a double bond is proved by addition of one molecule of hydrochloric acid, the dry gas precipitating from cooled oil of turpentine a compound of the formula $C_{10}H_{16} \cdot HCl$, called "artificial camphor," which resembles camphor both in appearance and odour. Pinene also readily forms an addition-product with nitrosyl chloride.

Pinene has the formula



Pinene

The presence of a tetramethylene-ring is assumed in order to explain the constitution of oxidation-products of pinene, such as *pinonic acid* and *pinic acid,* and for other reasons. Under the influence of benzenesulphonic acid, pinene in acetic-acid solution combines with one molecule of water to form terpineol, the tetramethylene-ring being opened. This transformation indicates the position of the double bond.

CAMPHORS.

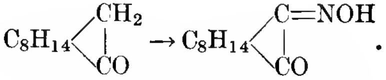
418. Ordinary *camphor,* $C_{10}H_{16}O$, is the most important member of the camphane-group. No other organic compound has been so much investigated, or from such widely different points of view. Ordinary, dextro-rotatory, "Japan camphor" is obtained by the steam-distillation of the bark of the camphor-tree. It forms a white, soft, crystalline mass of characteristic odour, and sublimes even at the ordinary temperature. It melts at 175·7°, and boils at 209·1°.

The camphor-odour is characteristic of many compounds theoretically derived by substitution of all the hydrogen atoms attached to a single carbon atom; that is, of tertiary compounds. Very few of the relations between odour and chemical constitution have been discovered, but many compounds containing a double bond are characterized by their pleasant aroma, while that of substances with a triple bond is frequently disagreeable.

Camphor is a saturated ketone—saturated because it does not yield addition-products, and a ketone because it forms an oxime. Reduction converts it into a secondary alcohol, *borneol* or "Borneo camphor":

$$\underset{\text{Camphor}}{C_9H_{16}\cdot CO}+2H = \underset{\text{Borneol}}{C_9H_{16}\cdot CHOH}.$$

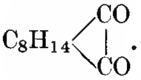
In addition to the carbonyl-group, the camphor molecule contains a methylene-group, for it has the properties of compounds with the group $—CH_2\cdot CO—$. As explained in **200**, the hydrogen of such a methylene-group can be replaced by the oxime-group by the action of amyl nitrite and hydrochloric acid. Camphor reacts similarly, these reagents converting it into iso*nitrosocamphor*, which melts at 153°:



$$C_8H_{14}\left<\begin{matrix}CH_2\\ |\\ CO\end{matrix}\right. \rightarrow C_8H_{14}\left<\begin{matrix}C{=}NOH\\ |\\ CO\end{matrix}\right. .$$

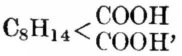
Camphor *iso*Nitrosocamphor

Elimination of the oxime-group from *iso*nitrosocamphor yields *camphor-quinone*,



$$C_8H_{14}\left<\begin{matrix}CO\\ |\\ CO\end{matrix}\right. .$$

On treatment with hydrogen peroxide, this compound readily takes up 2OH, forming *camphoric acid*,

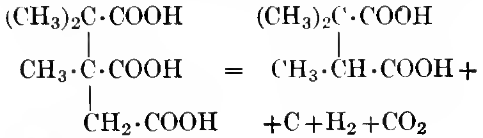


$$C_8H_{14}<\begin{matrix}COOH\\ COOH\end{matrix},$$

which can also be obtained directly from camphor by oxidation with nitric acid. It follows that, given the constitution of camphoric acid, that of camphor can be inferred.

Ordinary camphoric acid is dextro-rotatory, and melts at 187°. Four optically active camphoric acids are known: dextro-rotatory and lævo-rotatory camphoric acid, and dextro-rotatory and lævo-rotatory iso*camphoric acid*, with the same constitution as camphoric acid. These facts indicate that the molecule of camphoric acid must contain two dissimilar asymmetric C-atoms (**191**).

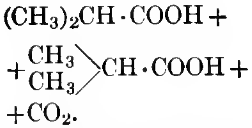
Energetic oxidation converts camphoric acid into the tribasic, optically active *camphoronic acid*, the constitution of which follows from its synthesis, and from its decomposition-products when submitted to dry distillation. This process decomposes it into trimethylsuccinic acid, *iso*butyric acid, carbon dioxide, and carbon:



$$\begin{array}{c} (CH_3)_2C\cdot COOH \\ | \\ CH_3\cdot C\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} = \begin{array}{l} (CH_3)_2C\cdot COOH \\ \quad | \\ CH_3\cdot CH\cdot COOH + \\ +C+H_2+CO_2 \end{array}$$

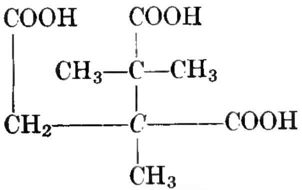
Camphoronic acid

and

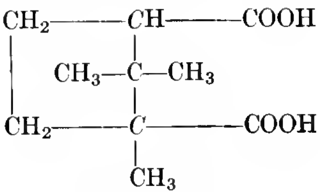


$$\begin{array}{l} (CH_3)_2CH\cdot COOH + \\ +\begin{array}{c}CH_3\\CH_3\end{array}\!\!>CH\cdot COOH + \\ +CO_2. \end{array}$$

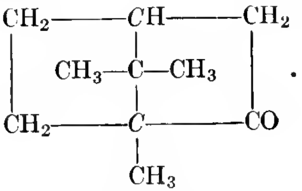
From these facts it is possible to deduce a formula for camphoric acid, which also accounts for its other properties:



Camphoronic acid



Camphoric acid

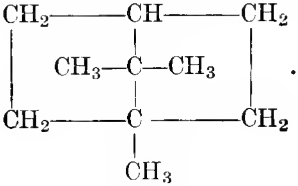


Camphor

This structural formula for camphor was originally proposed by Bredt. His view has been confirmed by the synthesis of camphor, effected by W. H. Perkin, Jun. and Thorpe, but the details of the processes involved are beyond the scope of this work. The formula of camphor contains two dissimilar, asymmetric C-atoms, represented in *italic*.

The position of the carbonyl-group in camphor follows from its conversion into carvacrol by the action of iodine: in this compound the hydroxyl-group is in the *ortho*-position to the methyl-group (416).

Borneol contains a CHOH-group instead of the CO-group present in camphor. By replacement of the hydroxyl-group by iodine, it yields bornyl iodide, which can be reduced to camphane:



Camphane

According to the formula, the conversion of CO into CH_2 should destroy the asymmetry of both the asymmetric C-atoms of camphor, and camphane is, in fact, optically inactive.

The formula of camphor contains an *iso*propyl-group, and therefore accounts for the conversion of camphor into cymene by heating with phosphorus pentasulphide.

BENZENE-NUCLEI LINKED TOGETHER DIRECTLY, OR INDIRECTLY BY CARBON.

419. The simplest possible compound of this nature is one containing two benzene-nuclei directly linked together. In addition, there are compounds with the benzene-nuclei indirectly connected by a carbon atom, or by a chain of carbon atoms. A few typical examples will be cited.

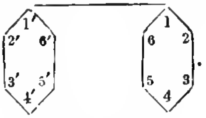
Diphenyl, $C_6H_5 \cdot C_6H_5$.

420. *Diphenyl* can be best prepared by heating iodobenzene with finely-divided copper at 220°. Another method for the preparation of the derivatives of diphenyl, the conversion of hydrazobenzene into benzidine, is mentioned in 324. On removal of the amino-groups from benzidine by means of the diazo-reaction, diphenyl remains. This method of formation also affords a proof of the constitution of benzidine.

Oxidation converts diphenyl into benzoïc acid. This reaction and its synthesis prove its constitution.

Diphenyl forms large, tabular, colourless crystals, readily soluble in alcohol and ether. It melts at 71°, and boils at 254°.

The isomeric substitution-products of diphenyl are much more numerous than those of benzene, as the scheme indicates:



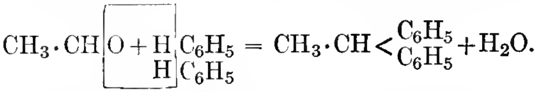
Diphenyl

A monosubstitution-product can exist in three isomeric forms, the substituent being in the *ortho*-position, *meta*-position, or *para*-position to the bond between the benzene-nuclei. In a disubstitution-product, both substituents may be linked to the same benzene-nucleus, or to different benzene-nuclei, and so on.

Benzidine is of technical importance, because many of the azo-dyes are derived from it.

Diphenylmethane, $C_6H_5\cdot CH_2\cdot C_6H_5$.

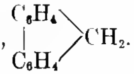
421. *Diphenylmethane* can be obtained from benzyl chloride, $C_6H_5\cdot CH_2Cl$, or from methylene chloride, CH_2Cl_2, by means of benzene and aluminium chloride. Its homologues are obtained by the action of benzene and concentrated sulphuric acid upon aldehydes. Thus, acetaldehyde yields *unsymmetrical diphenylethane:*

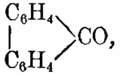
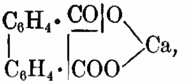


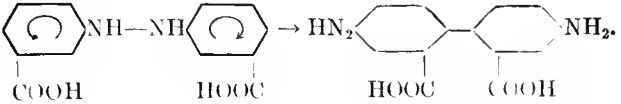
$$CH_3\cdot CH\begin{array}{|l|}\hline O+H\\ \quad\;\;H\\\hline\end{array}\begin{array}{l}C_6H_5\\C_6H_5\end{array} = CH_3\cdot CH<\begin{array}{l}C_6H_5\\C_6H_5\end{array}+H_2O.$$

When derivatives of benzene are substituted for benzene itself, many derivatives of diphenylmethane can be obtained by the application of these syntheses.

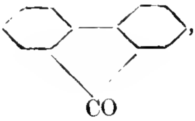
Diphenylmethane is crystalline. It melts at 26°, boils at 262°, and has an odour resembling that of orange-peel. Oxidation with chromic acid converts into benzophenone (336).

422. A derivative of diphenylmethane, in which the benzene-nuclei are directly linked, is *fluorene*,  $\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\!\!>CH_2$. It is formed by leading the vapour of diphenylmethane through a red-hot tube. From alcohol it crystallizes in leaflets: the crystals are fluorescent, a circumstance which gave this compound its name. It melts at 113°, and boils at 295°. It yields red needles with picric acid.

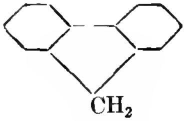
The constitution of fluorene is thus established. It is converted by the action of oxidizing agents into *diphenyleneketone*, the formula of which,  $\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\!\!>CO$, is established by its formation when the calcium salt of *diphenic acid*,  $\begin{array}{l}C_6H_4\cdot\underline{CO}|O\\|\qquad\quad\;|\\C_6H_4\cdot|COO\end{array}\!\!>Ca$, is distilled. Diphenic acid, for its part, is obtained from *m*-hydrazobenzoïc acid by the benzidine-transformation (324), and subsequent elimination of the amino-groups:



It follows that the carbonyl-group in diphenyleneketone is linked at the *ortho*-position in both the benzene-nuclei: it has, therefore, the structure

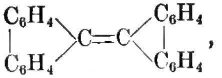


, and fluorene itself



This view receives confirmation from the fact that phthalic acid is the only product obtained by its oxidation.

The hydrogen of the CH_2-group in fluorene can be replaced by potassium. Oxidation of fluorene with lead oxide at 310°–330° yields *di-diphenylene-ethylene*,



$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right\rangle C=C\left\langle\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right.,$$

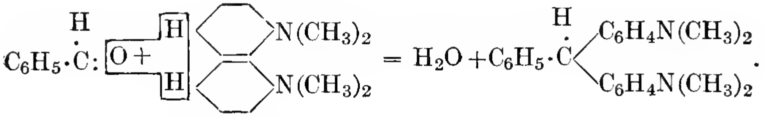
which melts at 188°. It is characterized by its deep-red colour, most hydrocarbons being colourless, at least in thin layers (295).

Triphenylmethane and its Derivatives.

423. *Triphenylmethane,* $CH(C_6H_5)_3$, is formed from benzal chloride, $C_6H_5{\cdot}CHCl_2$, by the action of benzene and aluminium chloride; from benzaldehyde and benzene in presence of a dehydrating agent, such as zinc chloride; and from the interaction of chloroform and benzene in presence of aluminium chloride. It crystallizes in beautiful, colourless prisms melting at 93°. Its boiling-point is 359°.

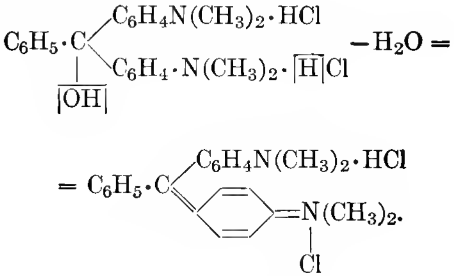
A series of important dyes, the *rosanilines,* is derived from this hydrocarbon. Triphenylmethane itself is not employed as a basis for their preparation, but simpler substances which are converted into its derivatives. The formation of the dye takes place in three stages: *malachite-green* furnishes an example.

When benzaldehyde and dimethylaniline are heated with zinc chloride, *tetramethyldiaminotriphenylmethane* is formed:



The carbon atom of the aldehyde group, therefore, furnishes the "methane carbon atom" of triphenylmethane.

This substance is also called *leucomalachite-green.* It is converted by oxidation with PbO_2, in hydrochloric-acid solution, into the corresponding carbinol, $\underset{OH}{C_6H_5\dot{C}[C_6H_4N(CH_3)_2]_2}$, a colourless, crystalline substance, like the leuco-compound from which it is derived. Being an amino-base, it is capable of yielding salts: thus, it dissolves in acids with the formation of colourless salts. When such a solution is warmed, water is eliminated, and the deep-green dye produced. The dye, either as a double salt with zinc chloride, or as an oxalate, is known as *malachite-green.* The elimination of water may be represented in several ways; it is usually supposed to take place thus:

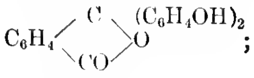


Quinonoid form

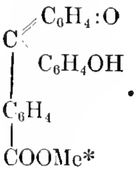
This "quinonoid reaction" is analogous to the formation of quinone from quinol, in which the colourless quinol is converted into the deep-yellow quinone.

The conversion into a quinonoid form also explains many other instances of the formation of coloured substances; for example, the conversion of the colourless phenolphthaleïn (369) into its red metallic derivative.

Bernthsen has proved that this indicator in the colourless state is a lactone,



but that its red salts are derivatives of a carboxylic acid containing a quinonoid-group,



When the phenolphthaleïn is regenerated from this salt by the action of an acid, it changes, like the *pseudo*-acids (311), into the colourless lactone-form, the transformation in this case being instantaneous

The distinguishing characteristic of the group $:C_6H_4:O$ is its strongly marked chromophore character.

424. The three stages necessary to the formation of the dye, may, therefore, be defined as follows.

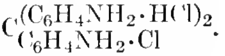
1. Formation of a *leuco-base* (colourless), a derivative of

$$HC(C_6H_4NH_2)_3.$$

2. Formation of a *colour-base* (colourless), a derivative of

$$HO\cdot C(C_6H_4NH_2)_3.$$

3. Formation of the *dye*, a derivative of



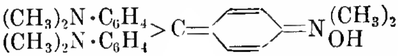
$$C\begin{matrix}(C_6H_4NH_2\cdot HCl)_2\\ C_6H_4NH_2\cdot Cl\end{matrix}.$$

Reduction reconverts the dyes into their leuco-bases, two hydrogen atoms being taken up during the reaction.

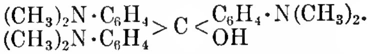
---

* Me represents one equivalent of a metal.

Crystal-violet (hexamethyltriaminotriphenylmethane) furnishes an excellent example of a phenomenon also exhibited by other analogous basic substances. When an equivalent quantity of an alkali is added to a salt of crystal-violet, the liquid still remains coloured, has a strong alkaline reaction, and conducts an electric current. On standing, the solution slowly becomes colourless, when it is no longer alkaline, and its electric conductivity has fallen to that of the alkali-metal salt present in the liquid. The liquid now contains a colour-base. These phenomena are analogous to the conversion of acids into *pseudo*-acids (311). For this reason the colour-base may be looked upon as a pseudo-*base*. Thus, on addition of the equivalent quantity of NaOH to crystal-violet, the true base,



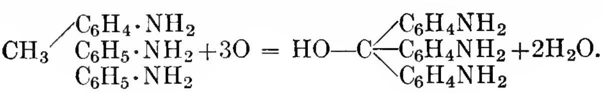
is at first present in the solution: after standing for several hours at 25°, however, this true base changes into the colour-base (*pseudo*-base),



$$\begin{matrix}(CH_3)_2N\cdot C_6H_4\\(CH_3)_2N\cdot C_6H_4\end{matrix}\!>C<\!\begin{matrix}C_6H_4\cdot N(CH_3)_2.\\OH\end{matrix}$$

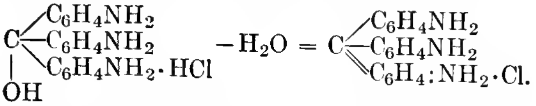
Hantzsch has been able to identify as *pseudo*-bases substances other than those mentioned.

425. *Pararosaniline* is obtained by the oxidation of a mixture of p-toluidine (1 molecule) and aniline (2 molecules) by means of arsenic acid or nitrobenzene. The methyl-group of toluidine thus furnishes the "methane carbon atom" of triphenyl methane:



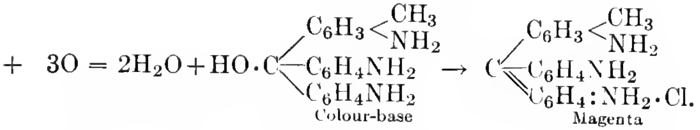
$$CH_3\!\begin{matrix}\diagup C_6H_4\cdot NH_2\\ C_6H_5\cdot NH_2\\ C_6H_5\cdot NH_2\end{matrix}+3O = HO—C\!\begin{matrix}\diagup C_6H_4NH_2\\ —C_6H_4NH_2\\ \diagdown C_6H_4NH_2\end{matrix}+2H_2O.$$

This colour-base dissolves in acids, forming a red dye: it can be reprecipitated by alkalis. It is transformed by reduction with zinc-dust and hydrochloric acid into *paraleucaniline*, $HC(C_6H_4NH_2)_3$, a colourless, crystalline substance which melts at 148°, and is reconverted into the colour-base by oxidation. The constitution of paraleucaniline is indicated by the formation of triphenylmethane on elimination of its amino-groups by diazotization. On the other hand, paraleucaniline can be obtained by the nitration of triphenylmethane, and subsequent reduction of the trinitro-derivative thus formed. Paraleucaniline is converted by oxidation into triaminotriphenylcarbinol, which, like malachite-green, loses water under the influence of acids, forming the dye:



Another important dye related to triphenylmethane is *rosaniline*. Its preparation is similarly effected by oxidizing a mixture of aniline, *o*-toluidine, and *p*-toluidine in equimolecular proportions with arsenic acid, mercuric nitrate, or nitrobenzene. In this reaction the methane carbon atom is obtained from *p*-toluidine as follows:

$$\underset{p\text{-Toluidine}}{NH_2\cdot C_6H_4\cdot CH_3} + \underset{o\text{-Toluidine}}{C_6H_4(CH_3)NH_2} + C_6H_5\cdot NH_2 \quad +$$



The chloride of the rosaniline colour-base, obtained by combination with one equivalent of hydrochloric acid and elimination of one molecule of water, is called *magenta*. This substance forms beautiful green crystals with a metallic lustre, which dissolve in water, yielding a solution of an intense deep-red colour.

The colour of the magenta solution is due to the univalent cathion, $(C_{20}H_{20}N_3)$, because such solutions are almost completely ionized, as the slight increase of their molecular conductivity on further dilution shows. Moreover, the solutions of all the magenta salts—chloride, bromide, sulphate, etc.—exhibit the same absorption-spectrum for solutions of equimolecular concentration, an indication of the presence of a constituent common to all of them (the cathion).

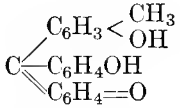
The salts containing three equivalents of acid are yellow, the red, univalent cathion having been converted into the yellow, tervalent cathion: in consequence, magenta dissolved in excess of hydrochloric acid yields a nearly colourless solution. These salts are, however, very readily hydrolyzed: the red colour reappears when this solution in hydrochloric acid is poured into water.

Many derivatives of pararosaniline and rosaniline are known in which the hydrogen atoms of the amino-group have been replaced by alkyl-radicals. They are all dyes. The violet colour becomes deeper as the number of methyl-groups present increases (364). *Pentamethylpararosaniline* has the trade-name "methyl-violet." When one hydrogen atom in each of the amino-groups of rosaniline is replaced by phenyl, a blue dye is formed, called "aniline-blue."

The alkyl-groups were formerly introduced into pararosaniline in the ordinary way, by means of an alkyl chloride or even iodide. These methods have since been superseded by others, better suited to the preparation of the alkyl-derivatives. For example, methyl-violet is obtained by the oxidation of dimethylaniline with potassium chlorate and cupric chloride, the methane carbon atom being obtained from one of the methyl-groups.

Aniline-blue, or *triphenylrosaniline hydrochloride*, is got by heating rosaniline with aniline and a weak acid, such as benzoïc acid, whereby the amino-groups in the rosaniline are replaced by anilino-groups, the ammonia set free entering into combination with the acid. This process is analogous to the formation of diphenylamine from aniline hydrochloride and aniline (315).

426. Dyes formed from hydroxyl-derivatives of triphenylmethane are also known, but are much less valuable than those just described, on account of the difficulty of fixing them. *Rosolic acid*,



obtained from rosaniline by diazotization, is an example of such dyes.

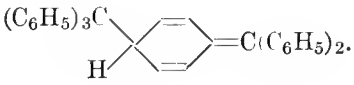
Malachite-green and the pararosaniline and rosaniline dyes colour wool and silk directly, and calico after it has been mordanted.

It is stated in 362 that the fixing of dyes upon vegetable or animal fibres must be regarded as a chemical combination of the compounds contained in the fibre with the dye, analogous to the formation of salts. The following is a proof. The colour-base of rosaniline is colourless: when, however, wool or silk is immersed in its colourless solution, it becomes gradually coloured, as though an acid had been added. This phenomenon can only be explained by supposing that a compound in the fibre unites with the colourless base, forming with it a salt of the same colour as a solution of the dye in water.

The phthaleïns, dyes related to triphenylmethane, have been mentioned (369).

427. Gomberg has investigated the action of zinc upon a benzene solution of *triphenylchloromethane:* zinc chloride separates, and the solution contains a compound which can be precipitated by addition of acetone or ethyl formate. This compound he regards as *triphenylmethyl,* $(C_6H_5)_3C—$, with one free linking.

If Gomberg's view is correct, this body affords the first example of a compound with a tervalent carbon atom. Its power of forming addition-products is remarkable. It is at once oxidized by atmospheric oxygen to a *peroxide,* $(C_6H_5)_3C—O—O—C(C_6H_5)_3$. It decolourizes iodine-solution instantaneously, forming *triphenylmethyl iodide.* It yields addition-products with many compounds. Against the view that it contains a tervalent carbon atom is the fact that the molecular weight indicated by the cryoscopic method is twice as great as that required by the empirical formula. Although this result may be due to association of the triphenylmethyl molecules, as sometimes happens with unsaturated compounds, the possibility of Gomberg's compound being hexaphenylethane, $(C_6H_5)_3C \cdot C(C_6H_5)_3$, must not be overlooked. The choice lies between two very novel explanations: either the compound is triphenylmethyl, and is the only known body with a tervalent carbon atom; or it is hexaphenylethane, which would involve a severance of the linking between the ethane-carbon atoms under circumstances such as have never been observed in organic chemistry. A satisfactory decision between the two views has not yet been attained. Quinonoid formulæ have also been suggested for triphenylmethyl; for example,



Dibenzyl and its Derivatives.

428. *Dibenzyl*, $C_6H_5\cdot CH_2\cdot CH_2\cdot C_6H_5$, can be obtained by the action of sodium upon benzyl chloride:

$$C_6H_5\cdot CH_2\boxed{Cl + Na_2 + Cl}CH_2\cdot C_6H_5 = C_6H_5\cdot CH_2\cdot CH_2\cdot C_6H_5 + 2NaCl.$$

This method of formation shows it to be *symmetrical diphenylethane*. It melts at 52°.

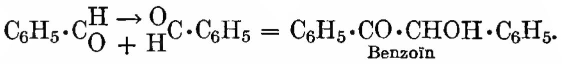
Symmetrical diphenylethylene, $C_6H_5\cdot CH:CH\cdot C_6H_5$, M.P. 125°, is called *stilbene*. It can be obtained by various methods: for example, by heating an aqueous solution of phenylsodionitromethane, which is thereby decomposed into stilbene and sodium nitrite:

$$2C_6H_5\cdot CH:NO\cdot ONa = C_6H_5\cdot CH:CH\cdot C_6H_5 + 2NaNO_2.$$

Stilbene forms an addition-product with bromine, from which *tolan*, $C_6H_5\cdot C\equiv C\cdot C_6H_5$, is produced by elimination of 2HBr. Tolan can be reconverted into stilbene by careful reduction.

p-*Diaminostilbene*, $NH_2\cdot C_6H_4\cdot CH:CH\cdot C_6H_4\cdot NH_2$, can be obtained by treatment of *p*-nitrobenzyl chloride, $ClH_2C\cdot C_6H_4\cdot NO_2$, with alcoholic potash, and subsequent reduction of the p-*dinitrostilbene* thus formed. It is used as a basis for the preparation of certain dyes.

Derivatives of dibenzyl are got by the condensation of benzaldehyde in presence of potassium cyanide. For example, *benzoïn* is thus formed:

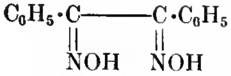


$$C_6H_5\cdot C\overset{H}{\underset{O}{}}\overset{\rightarrow}{\underset{+}{}}\overset{O}{\underset{H}{}}C\cdot C_6H_5 = \underset{\text{Benzoïn}}{C_6H_5\cdot CO\cdot CHOH\cdot C_6H_5}.$$

It has the character of a keto-alcohol, since it takes up two hydrogen atoms, with formation of a dihydric alcohol, *hydrobenzoïn*, $C_6H_5\cdot CHOH\cdot CHOH\cdot C_6H_5$. On oxidation it yields a diketone, *benzil*, $C_6H_5\cdot CO\cdot CO\cdot C_6H_5$. Benzoïn contains the group $—CHOH\cdot CO—$, which is present in the sugars (203). It also possesses properties characteristic of the sugars: thus, it reduces an alkaline copper solution, and yields an osazone.

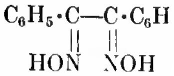
Benzil is a yellow, crystalline substance. As a diketone it unites with two molecules of hydroxylamine to form a dioxime.

429. *Benzildioxime* exists in three isomeric forms, the number indicated by the stereoisomerism of nitrogen derivatives (337):



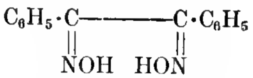
$$\begin{array}{ccc} C_6H_5\cdot C & \text{———} & C\cdot C_6H_5 \\ \| & & \| \\ NOH & & NOH \end{array}$$

*amphi*Benzildioxime



$$\begin{array}{ccc} C_6H_5\cdot C & — & C\cdot C_6H \\ \| & & \| \\ HON & & NOH \end{array}$$

*anti*Benzildioxime

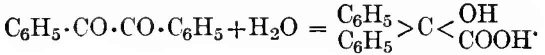


$$\begin{array}{ccc} C_6H_5\cdot C & \text{————} & C\cdot C_6H_5 \\ \| & & \| \\ NOH & & HON \end{array}$$

*syn*Benzildioxime

One of these oximes readily yields an anhydride, and is therefore assumed to have the two hydroxyl-groups in close proximity, the *syn*-formula. One of the other dioximes is the most stable of the three compounds, and can be obtained by various means. The third dioxime can be easily transformed into this stable modification. It is probable that the stable dioxime has the symmetrical or *anti*-formula, so that the *amphi*-formula must be that of the unstable modification.

When heated with alcoholic potash, benzil takes up one molecule of water, undergoing an intramolecular transformation, with production of *benzilic acid*, a reaction analogous to the formation of pinacolin from pinacone (156):



$$C_6H_5\cdot CO\cdot CO\cdot C_6H_5+H_2O = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}>C<\begin{matrix} OH \\ COOH \end{matrix}.$$

Benzilic acid

CONDENSED BENZENE-RINGS.

430. *Condensed-ring compounds* contain two or more closed chains, with C-atoms common to both. Such compounds are present in the higher-boiling fractions of coal-tar (293). Next to the phenols, *naphthalene* is the principal constituent of the second fraction, carbolic oil, and of the third fraction, creosote-oil. The anthracene-oil contains *anthracene* and *phenanthrene*, and other hydrocarbons. These three compounds and some of their derivatives will be described.

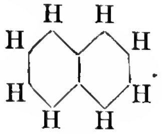
I. NAPHTHALENE, $C_{10}H_8$.

431. *Naphthalene* is present in considerable proportion in coal-tar, from which it is readily obtained pure. On cooling, the crude crystals of naphthalene precipitate from the fraction distilling between 170° and 230° The liquid impurities are pressed out, and are further eliminated by conversion into non-volatile sulphonic acids on warming the crude product with small quantities of concentrated sulphuric acid, and distilling with steam or subliming. The process yields pure naphthalene.

Naphthalene crystallizes in shining plates, melting at 80°, and boiling at 218° It is insoluble in water, but readily soluble in hot alcohol and ether: it dissolves to a very small extent in cold alcohol. It has a characteristic odour, and is very volatile. It is always present in coal-gas, the illuminating power of which is to a large extent due to its presence. It is extensively employed in the manufacture of dyes.

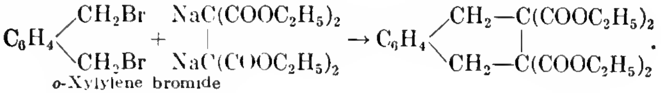
The formation of naphthalene on passing the vapours of many compounds through a red-hot tube, a process somewhat similar to that which takes place in the retorts of the gas-works (293), explains its occurrence in coal-tar.

The constitution of naphthalene is proved in 399 to be



This view is confirmed by two syntheses.

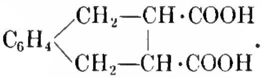
1. *o*-Xylylene bromide is converted by treatment with tetraethyl disodioethanetetracarboxylate into *tetraethyl hydronaphthalenetetracarboxylate:*



$$C_6H_4\begin{cases}CH_2Br\\CH_2Br\end{cases} + \begin{array}{l}NaC(COOC_2H_5)_2\\ \quad|\\ NaC(COOC_2H_5)_2\end{array} \rightarrow C_6H_4\begin{cases}CH_2-C(COOC_2H_5)_2\\ \qquad\ \ |\\ CH_2-C(COOC_2H_5)_2\end{cases}.$$

o-Xylylene bromide

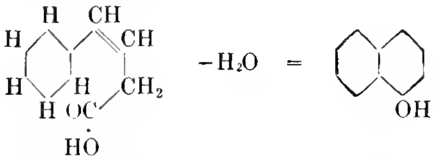
On saponification, this compound loses two molecules of carbon dioxide, forming *hydronaphthalenedicarboxylic acid:*



$$C_6H_4\begin{cases}CH_2-CH\cdot COOH\\ \qquad\ \ |\\ CH_2-CH\cdot COOH\end{cases}.$$

The silver salt of this acid readily gives up two molecules of carbon dioxide and two atoms of hydrogen, yielding naphthalene.

2. On heating, phenylvinylacetic acid is converted into *α-naphthol,* a hydroxy-derivative of naphthalene:



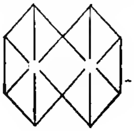
Phenylvinylacetic acid

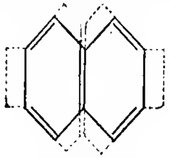
α-Naphthol

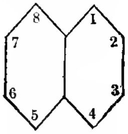
Naphthalene behaves in all respects as an aromatic hydrocarbon. With nitric acid it yields a nitro-derivative; with sulphuric acid a sulphonic acid: its hydroxyl-derivatives have the phenolic character: the amino-compounds undergo the diazo-reaction: etc.

For naphthalene, as for benzene (289), no formula indicating its internal structure and satisfactorily accounting for its properties has been proposed.

Formula I. (Fig. 81) is analogous to the centric formula for benzene: it is difficult to represent its configuration in space.


I
FIG. 81.


II
FIG. 82.



III
FIG. 83.

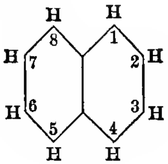
FIG. 81.—CENTRIC NAPHTHALENE-FORMULA.
FIG. 82.—THIELE'S NAPHTHALENE-FORMULA.
FIG. 83.—SIMPLE NAPHTHALENE-FORMULA.

THIELE has suggested formula II. (Fig. 82), with inactive double linkings (289), and of those put forward it seems to give the best expression to the properties of naphthalene. The question of what formula most accurately represents the internal structure of the naphthalene molecule is, however, of no practical importance, for the simple scheme III. (Fig. 83), which leaves the problem unsolved, fully accounts for the isomerism of the derivatives of naphthalene.

As with benzene, partial hydrogenation of naphthalene changes its characteristic aromatic character; for *naphthalene dihydride*, $C_{10}H_{10}$, adds bromine as readily as compounds with double linkings.

432. Naphthalene yields a much greater number of substitution-products than benzene, the number obtained corresponding to those theoretically possible for a compound with the formula in 431. This fact supports the constitution indicated.

A compound of the formula

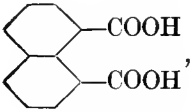


must yield two isomeric monosubstitution-products. Substitution can take place at a carbon atom directly linked to one of the two C-atoms common to both rings (1, 4, 5, or 8), or at one of the others (2, 3, 6, or 7), which are also similar to one another. Two series of monosubstitution-products are in fact known: those in which the hydrogen at 1, 4, 5, or 8 has been replaced are called α-derivatives; when hydrogen is substituted at 2, 3, 6, or 7, the products are termed β-derivatives.

A great number of disubstitution-products is possible: for two similar substituents it is 10, and for two dissimilar substituents 14. Many of them have been obtained. The ten isomerides are denoted by the numbers

1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 2:3, 2:6, 2:7.

In any other arrangement the grouping is identical with one of these: thus, 2:5 = 1:6, and 3:6 = 2:7, etc. For three similar substituents the number of possible isomerides is much greater, and still greater for three dissimilar ones. The disubstitution-products with the substituents in the same ring are called *ortho*, *meta*, and *para*. When they are in different rings, the compounds are usually distinguished by numbers, or sometimes by letters: thus, a compound 4:5 is also denoted by $\alpha\alpha'$, and one 3:6 by $\beta\beta'$. The positions 1:8 and 4:5 are also called the *peri*-positions: in certain respects they resemble the *ortho*-positions. For example, peri-*naphthalenedicarboxylic acid,*



,

resembles *o*-phthalic acid in its ability to form an anhydride.

433. On account of the great number of isomerides, the orientation of naphthalene derivatives is sometimes difficult, and the positions occupied by the substituents in many compounds are still uncertain. The same method of orientation is employed as for the benzene derivatives, the conversion of compounds with side-chains in unknown positions into others with substituents in positions that have been determined.

Oxidation is another important aid in their orientation, and is employed to determine whether the substituents are attached to the same ring, or to different rings, as well as their position relative to one another. Thus, suppose the position of the nitro-groups in a dinitronaphthalene has to be determined. If it yields phthalic acid on oxidation, the two nitro-groups must be in union with the same ring, that one which has been removed by oxidation. If a dinitrophthalic acid is formed, this also proves that the two nitro-groups are linked to the same ring, and the orientation of these groups in this acid should indicate their relative position in the naphthalene derivative. Lastly, if oxidation yields a mononitrophthalic acid, one nitro-group is attached to each ring, and orientation of the mononitrophthalic acid obtained will determine the position of one of the nitro-groups.

Substitution-products.

434. The homologues of naphthalene — methyl-derivatives, ethyl-derivatives, etc.—are unimportant. They can be prepared by FITTIG's method, or that of FRIEDEL and CRAFTS (**294**, 1 and 2).

> *α-Methylnaphthalene* is a liquid, and boils at 240°–242°: β-methylnaphthalene is a solid, and melts at 32°. Both are present in coal-tar. On oxidation, they yield *α-naphthoïc acid* and *β-naphthoïc acid* respectively, which resemble benzoïc acid in their properties. They are converted into naphthalene by distillation with lime.

α-Chloronaphthalene and *α-bromonaphthalene* are respectively formed by the action of chlorine and bromine upon boiling naphthalene. Although their halogen atom is not so firmly linked as that in monochlorobenzene or monobromobenzene (**298**), they are not decomposed by boiling with alkalis. A similar stability characterizes the corresponding β-compounds, which are not obtained by the direct action of halogens upon naphthalene, but can be prepared from other β-compounds, such as amino-derivatives, sulpho-derivatives, etc., by the methods described under benzene (**341**, 4).

435. The product obtained by the action of concentrated nitric acid upon naphthalene is very important for the orientation of the naphthalene derivatives. It is *α-nitronaphthalene*, M.P. 61°, which is proved to belong to the α-series by its conversion into the same naphthol as is obtained from phenyl*iso*crotonic acid (**431**).

The position of the substituents in a great number of mono-substitution-products can be determined from a knowledge of that of the nitro-group in this nitronaphthalene, for the nitro-group can be reduced to an amino-group, which is replaceable by numerous atoms or groups by means of the diazo-reaction. If a mono-substituted naphthalene is known to be an α-compound, its isomeride must belong to the β-series.

α-Nitronaphthalene is a yellow, crystalline compound, and melts at 61°. The corresponding β-compound is similar, and melts at 79°

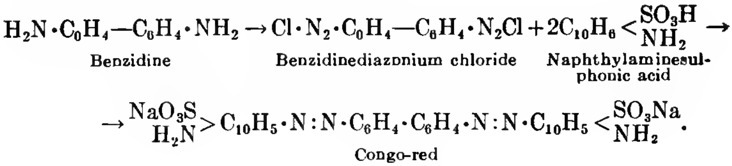
436. On heating naphthalene with concentrated sulphuric acid at a temperature not exceeding 80°, *α-naphthalenemonosulphonic acid* is chiefly formed: at 160° the β-acid is the principal product, owing to the conversion of the α-compound into its β-isomeride. Both are crystalline and very hygroscopic.

On fusion with caustic potash, the naphthalenesulphonic acids are converted into *naphthols*, $C_{10}H_7{\cdot}OH$, with properties very similar to those of phenol. They are present in coal-tar. *α-Naphthol* melts at 95°, and boils at 282°: *β-naphthol* melts at 122°, and boils at 288° The hydroxyl-group in these compounds can be replaced much more readily than that in phenol. They dissolve in alkalis. With ferric chloride α-naphthol yields a flocculent, violet precipitate: β-naphthol gives a green coloration, and a precipitate of *β-dinaphthol*, $HO{\cdot}C_{10}H_6{\cdot}C_{10}H_6{\cdot}OH$. The violet precipitate obtained with α-naphthol is possibly an iron derivative of *α-dinaphthol*.

437. *α-Naphthylamine* and *β-naphthylamine*, $C_{10}H_7{\cdot}NH_2$, can be obtained by the reduction of the corresponding nitro-derivatives, but are usually prepared by heating α-naphthol and β-naphthol respectively with the ammonia compound of zinc chloride or of calcium chloride. α-Naphthylamine is a solid and is also formed by heating naphthalene with sodamide, NH_2Na, above 200°, hydrogen being evolved. It melts at 50°, and has a fæcal-like odour: β-naphthylamine melts at 112°, and is nearly odourless. A mode of distinguishing between the isomerides is afforded by the fact that the salts of the α-compound, but not the β-compound, give a blue precipitate with ferric chloride and other oxidizing agents.

These bases are of technical importance, since the dyes of the *congo-group* and the *benzopurpurins* are derived from them, and possess the important property of dyeing unmordanted cotton.

Congo-red is formed by diazotizing benzidine, and treating the product with a sulphonic acid of naphthylamine. The dye is the sodium salt of the acid thus formed:



$$H_2N\cdot C_6H_4—C_6H_4\cdot NH_2 \rightarrow Cl\cdot N_2\cdot C_6H_4—C_6H_4\cdot N_2Cl + 2C_{10}H_6<\substack{SO_3H\\ NH_2} \rightarrow$$

Benzidine Benzidinediazonium chloride Naphthylaminesulphonic acid

$$\rightarrow \substack{NaO_3S\\ H_2N}>C_{10}H_5\cdot N:N\cdot C_6H_4\cdot C_6H_4\cdot N:N\cdot C_{10}H_5<\substack{SO_3Na\\ NH_2}.$$

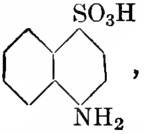
Congo-red

The acid itself is blue.

The benzopurpurins differ from congo-red only in having a methyl-group attached to each benzene-nucleus of the benzidine-group.

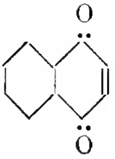
438. Among the polysubstituted naphthalene derivatives is *dinitro-α-naphthol,* obtained by the action of nitric acid upon the monosulphonic or disulphonic acid of α-naphthol. Its sodium salt is *Martius's yellow:* it dyes wool and silk directly a golden-yellow. Nitration of α-naphtholtrisulphonic acid yields dinitronaphtholsulphonic acid, the potassium salt of which is *naphthol-yellow:* it resists the action of light better than Martius's yellow.

Naphthionic acid is one of the longest-known naphthalene derivatives. It is 1:4-*naphthylaminesulphonic acid,*

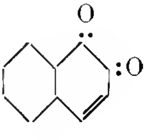


and results from the interaction of α-naphthylamine and sulphuric acid. It is crystalline, and only slightly soluble in water. It is manufactured for the preparation of congo-red and other dyes. Solutions of its salts display an intense reddish-blue fluorescence.

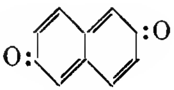
439. Three quinones of naphthalene are known:



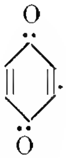
α



β



amphi



Benzoquinone

α-Naphthaquinone, $C_{10}H_6O_2$, is formed by the oxidation of many α-derivatives, and of some di-derivatives, of naphthalene. It is usually prepared from naphthalene itself by oxidation with a boiling solution of chromic acid in glacial acetic acid, a method of formation which has no parallel among those for the preparation of the corresponding benzene derivatives. It crystallizes from alcohol in deep-yellow needles, melting at 125°. On oxidation, it yields phthalic acid, proving both oxygen atoms to be attached to the same ring. With hydroxylamine it yields an oxime. Knowing the structure of α-naphthaquinone, it is possible to determine that of other di-derivatives. If, on oxidation, they yield this quinone by elimination of the substituents, they must be 1:4-derivatives.

β-Naphthaquinone, $C_{10}H_6O_2$, is formed by oxidation of 1:2-aminonaphthol.

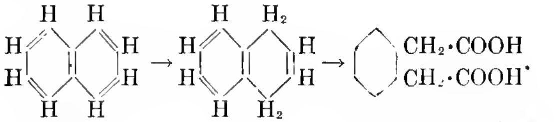
amphi-*Naphthaquinone*, or 2:6-*naphthaquinone*, is obtained by oxidation of a benzene-solution of the corresponding dihydroxynaphthalene with lead peroxide.

The structural formulæ indicate that only in the *amphi*-isomeride is the arrangement of the CO-groups relative to the double bonds similar to that in benzoquinone; and these two quinones are very similar in chemical character. Both oxidize at once a cold, dilute solution of hydriodic acid, turn ferrous ferrocyanide blue, and oxidize sulphurous acid. α-Naphthaquinone exhibits none of these characteristics, but resembles benzoquinone in odour and volatility. β-Naphthaquinone does not oxidize dilute hydriodic acid, but turns ferrous ferrocyanide blue, and oxidizes sulphurous acid. Like the *amphi*-derivative it is non-volatile, and therefore odourless. Each of the naphthaquinones has a red colour.

Addition-products.

440. Naphthalene and its derivatives yield addition-products somewhat more readily than the benzene derivatives.

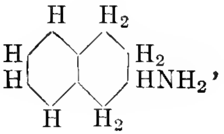
All the intermediate hydrogenation-products of naphthalene from *dihydronaphthalene*, $C_{10}H_{10}$, to *dodecahydronaphthalene*, $C_{10}H_{20}$, are known, each member having two hydrogen atoms more than its immediate predecessor. The first-named is obtained by the action of sodium and alcohol upon naphthalene. Oxidation converts it into *o-phenylenediacetic acid:*



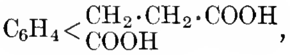
Naphthalene Dihydride *o*-Phenylenediacetic acid

Assuming that the formula given represents naphthalene, the **hydrogen** is added to the conjugated double linking at the positions 1:4.

When reduced with sodium and boiling amyl alcohol, β-naphthylamine yields a *tetrahydride*, $C_{10}H_{11}NH_2$, a compound with most of the properties characteristic of the aliphatic amines: it is strongly alkaline, absorbs carbon dioxide from the air, has an ammoniacal odour, and cannot be diazotized. All four hydrogen atoms are in union with the same ring as the amino-group,



since, on oxidation with potassum permanganate, the compound is converted into the *o*-carboxylic acid of dihydrocinnamic acid,

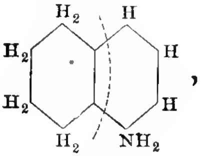


$$C_6H_4{<}\begin{matrix}CH_2{\cdot}CH_2{\cdot}COOH\\COOH\end{matrix},$$

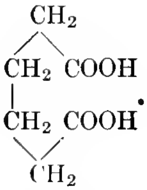
which must evidently result from a tetrahydride with the above structure if the oxidation takes place at the C-atom linked to the NH_2-group. Moreover, the hydrogen addition-product does not take up bromine, another proof that the four H-atoms are attached to the same benzene-nucleus. The entrance of two hydrogen atoms into each ring would produce a compound with double bonds, capable of yielding an addition-product with bromine.

The reduction-product may, therefore, be regarded as benzene with a saturated side-chain, $—CH_2·CH_2·CH(NH_2)·CH_2—$, linked to two *ortho*-C-atoms.

α-Naphthylamine can also be reduced by amyl alcohol and sodium, but the tetrahydride formed is different in character from that obtained from β-naphthylamine, for it possesses all the properties characteristic of the aromatic amines: it can be diazotized, and has no ammoniacal odour. Since, like β-naphthylamine, it forms no addition-product with bromine, its constitution is



which proves that the four hydrogen atoms in it likewise are in union with the same nucleus, but not the one linked to the amino-group. In support of this view are its completely aromatic character, and the fact that, on oxidation with potassium permanganate, the ring containing the amino-group is removed, with formation of adipic acid (164),



α-Naphthylamine tetrahydride must, therefore, be looked upon as aniline containing a saturated side-chain, $—CH_2·CH_2·CH_2·CH_2—$, linked to two *ortho*-C-atoms.

II. ANTHRACENE, $C_{14}H_{10}$.

441. *Anthracene* is present only in small proportions in coal-tar, varying between 0·25 and 0·45 per cent.; nevertheless, it is the basis of the manufacture of the important dyestuff, alizarin (**444** and **445**).

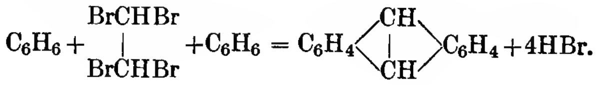
The so-called "50 per cent. anthracene," obtained by distilling anthracene-oil (**293**), is distilled with one-third of its weight of potassium carbonate from an iron retort. Certain impurities are thereby removed, among them *carbazole*, $\begin{matrix}C_6H_4\\ \vert\\ C_6H_4\end{matrix}\!\!>NH$, which is present in considerable proportion in the crude anthracene, and is thus converted into a non-volatile potassium derivative, $(C_6H_4)_2N\cdot K$. The distillate consists almost entirely of anthracene and phenanthrene: it is treated with carbon disulphide, which dissolves out the phenanthrene. By crystallization from benzene, the anthracene is obtained pure.

It crystallizes in colourless, glistening leaflets, with a fine blue fluorescence. It melts at 213°, and boils at 351°. It dissolves readily in boiling benzene, but with difficulty in alcohol and ether. With picric acid it yields a compound $C_{14}H_{10}\cdot C_6H_2(NO_2)_3OH$, melting at 138°.

On exposure to light, anthracene is transformed into *dianthracene*, which in the dark becomes depolymerized to anthracene, one of the rare instances of a reversible photochemical reaction:

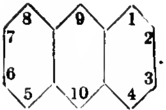
$$2C_{14}H_{10} \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} C_{28}H_{20}.$$

Several modes of preparing anthracene are known which give an insight into its constitution. One of these is its synthesis by Anschütz's method from benzene, aluminium chloride, and tetrabromoethane:



$$C_6H_6 + \begin{matrix}BrCHBr\\ \vert\\ BrCHBr\end{matrix} + C_6H_6 = C_6H_4\!\!<\!\begin{matrix}CH\\ \vert\\ CH\end{matrix}\!>\!\!C_6H_4 + 4HBr.$$

This synthesis proves that anthracene contains two benzene-nuclei united by the group C_2H_2, linked to two *ortho*-C-atoms of each, as proved for anthraquinone in **442**. Its constitutional formula is



Anthracene

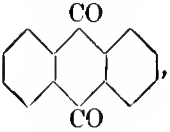
It follows that it must yield a very large number of isomeric substitution-products. Three monosubstitution-products are possible. Numbering the carbon atoms as in the formula, then 1=4=5=8, 2=3=6=7, and 9=10. Fifteen disubstitution-products with similar groups are possible. A very considerable number of anthracene derivatives is known, although it is small in comparison with the enormous number theoretically possible.

The orientation of the anthracene derivatives is effected similarly to those of naphthalene (433), oxidation and a study of the resulting products being an important aid.

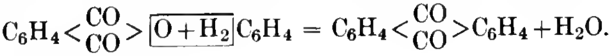
Substitution-products.

442. *Anthraquinone*, $C_{14}H_8O_2$, is one of the most important derivatives of anthracene, from which it is obtained by oxidation with such agents as nitric acid and chromic acid. Anthracene is so readily converted into anthraquinone by nitric acid that it is not possible to nitrate it.

Anthraquinone is proved to have the structure



since it is formed by the interaction of phthalic anhydride and benzene in presence of a dehydrating agent such as aluminium chloride:

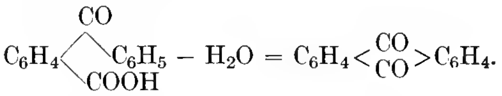


$$C_6H_4<\substack{CO\\CO}>\boxed{O+H_2}C_6H_4 = C_6H_4<\substack{CO\\CO}>C_6H_4+H_2O.$$

Phthalic anhydride

The reaction takes place in two stages: *o*-benzoylbenzoïc acid,

$C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot C_6H_5}{COOH}$, is first formed, and then loses one molecule of water, forming anthraquinone:

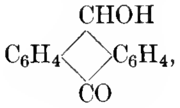


$$C_6H_4\genfrac{}{}{0pt}{}{CO}{COOH}C_6H_5 - H_2O = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4.$$

The constitutional formula of anthraquinone indicates that only two isomeric monosubstitution-products are possible. This has been verified by experiment—a further proof that the formula is correct.

443. Anthraquinone crystallizes from glacial acetic acid in light-yellow needles, melting at 277° At higher temperatures it sublimes very readily, forming long, sulphur-yellow prisms. It is very stable, and is not easily attacked by oxidizing agents, or by concentrated nitric acid or sulphuric acid.

The name anthra*quinone* is in some measure incorrect, for this substance lacks some of the properties characteristic of quinones, such as being easily reduced, great volatility, pungent odour, etc., and has much more the character of a diketone. With fused caustic potash it yields benzoïc acid, and with hydroxylamine an oxime. On warming with zinc-dust and caustic-soda solution, it forms *oxanthranol*,

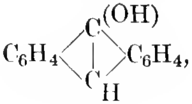


$$C_6H_4<\genfrac{}{}{0pt}{}{CHOH}{CO}>C_6H_4,$$

which in alkaline solution is converted into anthraquinone by atmospheric oxidation. Oxanthranol dissolves in alkalis, yielding a solution of a deep blood-red colour.

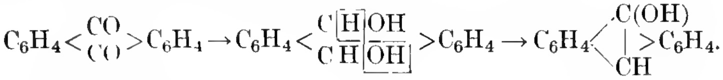
> This property of oxanthranol makes its formation a delicate test for anthraquinone. It is effected by warming the substance to be tested with zinc-dust and caustic-soda solution: if anthraquinone is present, a blood-red coloration is developed, and is destroyed by agitating the mixture with air.

On reduction with tin and hydrochloric acid, anthraquinone is converted into *anthranol*,



$$C_6H_4\left\langle\begin{matrix}C(OH)\\ | \\ CH\end{matrix}\right\rangle C_6H_4,$$

a substance of weak phenolic character, slightly soluble in cold and readily in boiling alkalis. Its formation is to be regarded as resulting from the elimination of water from an intermediate product, a dihydric alcohol:



$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4 \rightarrow C_6H_4<\begin{matrix}C\,\boxed{H}\,OH\\ C\,H\,\boxed{OH}\end{matrix}>C_6H_4 \rightarrow C_6H_4\left\langle\begin{matrix}C(OH)\\ | \\ CH\end{matrix}\right\rangle C_6H_4.$$

Anthraquinone Anthranol

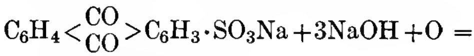
When anthraquinone is more strongly reduced, by heating with zinc-dust, it yields anthracene.

444. *Alizarin*, or dihydroxyanthraquinone, $C_{14}H_6O_2(OH)_2$, is the most important derivative of anthraquinone, and is a dye of a splendid red colour. It was formerly manufactured from madder-root, which contains a glucoside, *ruberythric acid*, $C_{26}H_{28}O_{14}$. When boiled with dilute sulphuric acid or hydrochloric acid, this glucoside yields dextrose and alizarin:

$$\underset{\text{Ruberythric acid}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Dextrose}}{2C_6H_{12}O_6} + \underset{\text{Alizarin.}}{C_{14}H_6O_2(OH)_2}.$$

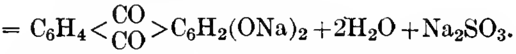
The dye is now prepared almost wholly by a synthetical method. It is one of the organic dyestuffs known in antiquity.

In preparing alizarin, the anthracene is first oxidized to anthraquinone with sodium dichromate and sulphuric acid. Heating with concentrated sulphuric acid at 100° converts various impurities into sulphonic acids, the anthraquinone remaining unchanged: on dilution, these sulphonic acids dissolve, so that pure anthraquinone is left after filtering. This is then heated to 160° with fuming sulphuric acid containing 50 per cent. of sulphur trioxide, the main product being the monosulphonic acid. Its sodium salt is only slightly soluble in water, and separates out when the acid is neutralized with sodium carbonate. On fusing with sodium hydroxide, the sulpho-group is replaced by hydroxyl. A second hydroxyl-group is simultaneously formed, its production being considerably facilitated by the addition to the reaction-mixture of potassium chlorate as an oxidizing agent:



$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot SO_3Na+3NaOH+O=$$

Sodium anthraquinone-monosulphonate



$$=C_6H_4<\substack{CO\\CO}>C_6H_2(ONa)_2+2H_2O+Na_2SO_3.$$

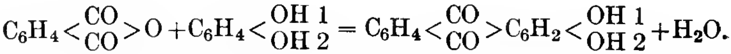
The dye is liberated from the sodium salt by addition of an acid.

Anthraquinone can be directly oxidized to alizarin by heating it with very concentrated aqueous alkali in presence of certain oxidizers, such as mercuric oxide, potassium chlorate, and so on.

Alizarin crystallizes in red prisms, and sublimes in orange needles, melting at 289°–290°. It is almost insoluble in water, and slightly soluble in alcohol. On account of its phenolic character, it dissolves in alkalis. It yields a diacetate. On distillation with zinc-dust, it is converted into anthracene, a reaction which gave the first insight into the constitution of alizarin.

The value of alizarin as a dye depends upon its power of forming with metallic oxides fine-coloured, insoluble compounds, called *lakes*. When a fabric is mordanted with one of these oxides, it can be dyed with alizarin, the colour depending on the oxide used. The ferric-oxide compound of alizarin is violet-black, the chromium-oxide compound claret-colour, the calcium-oxide compound blue, the aluminium-oxide and tin-oxide compounds various shades of red (Turkey-red), and so on.

445. The method by which alizarin is prepared proves it to be a derivative of anthraquinone, but the positions of the hydroxyl-groups have still to be determined. The formation of alizarin when phthalic anhydride is heated at 150° with catechol and sulphuric acid proves that both are in the same benzene-nucleus; and, since the hydroxyl-groups in catechol occupy the *o*-position, the same must be true of alizarin:

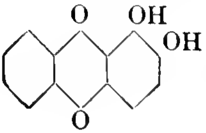


$$C_6H_4<\substack{CO\\CO}>O+C_6H_4<\substack{OH\ 1\\OH\ 2}=C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{OH\ 1\\OH\ 2}+H_2O.$$

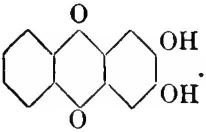
Phthalic anhydride — Catechol — Alizarin

It follows that the choice lies between the two structural formulæ

I.



and II.



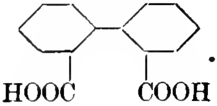
The result of nitration proves that formula I. is correct. Two isomeric mononitro-derivatives are obtained, each with the nitro-group in the same nucleus as the hydroxyl-groups, since both can be oxidized to phthalic acid. Formula I. alone admits of the formation of two such mononitro-derivatives, and must therefore be correct.

Other hydroxyl-derivatives of anthraquinone are also dyes, but only when two hydroxyl-groups are in the *o*-position to one another. Derivatives of anthraquinone containing hydroxyl-groups and amino-groups, or only amino-groups, are also valuable dyes.

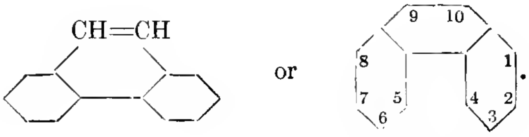
III. PHENANTHRENE, $C_{14}H_{10}$.

446. *Phenanthrene* is isomeric with anthracene, and is present with it in "anthracene-oil." They are separated by the method already described (**441**). It crystallizes in colourless, lustrous plates, which dissolve in alcohol more readily than anthracene, yielding a blue fluorescent solution. It melts at 96°, and boils at 340°.

On oxidation with chromic acid, it yields first *phenanthraquinone*, and then diphenic acid (**422**),

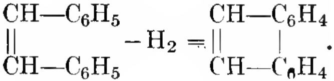


This reaction proves that phenanthrene possesses two benzene-nuclei directly linked to one another, and is therefore a diphenyl-derivative, and also a di-*ortho*-compound. Diphenyl with two hydrogen atoms substituted, $—C_6H_4·C_6H_4—$, or $—C_{12}H_8—$, differs from phenanthrene by C_2H_2. This must link together two *o*-positions, so that phenanthrene has the constitution



Phenanthrene

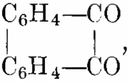
This structure finds support in the conversion of stilbene into phenanthrene, on passing its vapour through a red-hot tube, a method of formation analogous to that of diphenyl from benzene (420):



$$\begin{array}{l} CH-C_6H_5 \\ \| \\ CH-C_6H_5 \end{array} - H_2 = \begin{array}{l} CH-C_6H_4 \\ \| \quad\quad | \\ CH-C_6H_4 \end{array}.$$

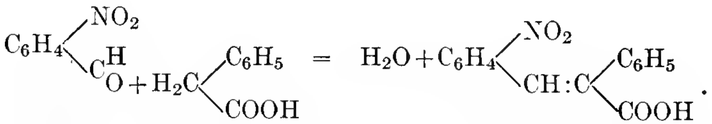
Stilbene Phenanthrene

In the formula of phenanthrene the group —CH=CH— and the four carbon atoms of diphenyl yield a third ring of six carbon atoms. This ring is distinguished from a true benzene-ring by the facts that the C_2H_2-group readily takes up bromine, and that on oxidation it behaves as an ordinary side-chain.



Phenanthraquinone, $\begin{array}{l} C_6H_4-CO \\ | \quad\quad\quad | \\ C_6H_4-CO \end{array}$, is an orange, crystalline substance, melting at 200°, and boiling without decomposition above 360°. Its diketonic character follows from its yielding di-derivatives with sodium hydrogen sulphite and with hydroxylamine. It is odourless, and non-volatile with steam.

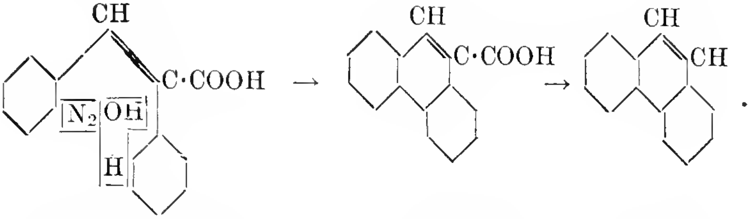
447. PSCHORR has discovered an important synthesis of phenanthrene and its derivatives, the condensation of *o*-nitrobenzaldehyde with phenylacetic acid by the PERKIN reaction (348):



$$C_6H_4\begin{cases} NO_2 \\ CH \\ \quad O \end{cases} + H_2C\begin{cases} C_6H_5 \\ COOH \end{cases} = H_2O + C_6H_4\begin{cases} NO_2 \\ CH:C\begin{cases} C_6H_5 \\ COOH \end{cases} \end{cases}.$$

o-Nitrobenzaldehyde Phenylacetic acid *a*-Phenyl-*o*-nitrocinnamic acid

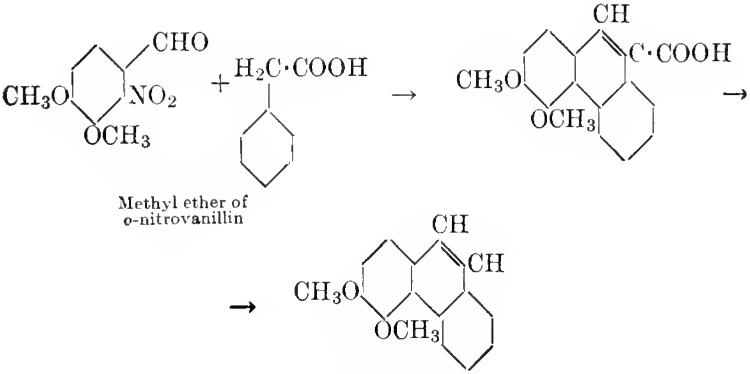
On diazotization of the corresponding amino-acid obtained by reduction, and treatment in sulphuric-acid solution with copper-dust (**341**), nitrogen and water are eliminated, and an almost quantitative yield of *β-phenanthrenecarboxylic acid* obtained:



Diazo-derivative of α-phenyl-o-aminocinnamic acid — Phenanthrene-carboxylic acid — Phenanthrene

On distillation, this acid loses carbon dioxide, forming phenanthrene.

When the methyl ether of o-*nitrovanillin* is substituted for *o*-nitrobenzaldehyde, there results a dimethoxyphenanthrene, *dimethylmorphol*, also formed by the breaking down of morphine (**478**):



Methyl ether of o-nitrovanillin

Dimethylmorphol

HETEROCYCLIC COMPOUNDS.

448. The compounds hitherto considered all contain a ring of carbon atoms only, and can be classed together as *homocyclic* compounds. It is mentioned in **281**, that ring-systems are also known possessing not only carbon atoms but also those of other elements. Substances with such rings are classed together as *heterocyclic* compounds. A few of them and their derivatives will be considered.

I. PYRIDINE, C_5H_5N.

449. *Pyridine* and some of its homologues are constituents of coal-tar. On mixing the "light oil" (**293**) with sulphuric acid, they are absorbed by the latter, and separate on addition of sodium carbonate in the form of a dark-brown, basic oil, from which pyridine and its homologues are obtained by fractional distillation. Prepared by this method, pyridine is never quite pure, always containing small proportions of its homologues.

Another source of pyridine is "Dippel's oil," a liquid of extremely disagreeable odour, obtained by the dry distillation of bones which have not been deprived of their fat. It is a very complicated substance, containing, in addition to the pyridine bases and quinoline, many other substances, such as nitriles, amines, and hydrocarbons.

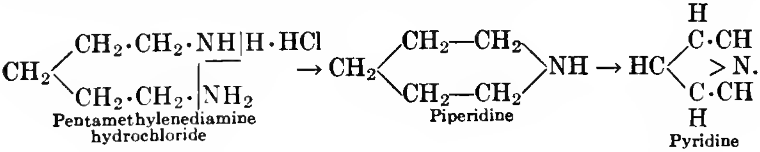
Pyridine is a colourless liquid boiling at 115°, and with a specific gravity of 1·0033 at 0°. It is miscible with water in all proportions, and has a weak alkaline reaction, colouring aqueous solutions of litmus only purple. It has a very characteristic odour, reminiscent of tobacco-smoke. It is very stable, being unattacked by boiling nitric acid or chromic acid. It reacts with sulphuric acid only at high temperatures, yielding a sulphonic acid. The halogens have very slight action on it. On very energetic reduction with hydriodic acid at 300°, it yields normal pentane and ammonia.

Being a base, it forms salts with acids, mostly readily soluble in water.

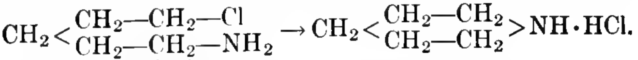
Pyridine ferrocyanide dissolves with difficulty, and is employed in the purification of the base. With platinum chloride, the hydrochloride yields a double salt, $(C_5H_5N)_2H_2PtCl_6$, freely soluble in water. When the solution is boiled, two molecules of hydrochloric acid are eliminated, with production of a yellow compound, $(C_5H_5N)_2PtCl_4$, which is only slightly soluble in water: the reaction affords a delicate test for pyridine.

The following test is also very delicate. On warming the base with methyl iodide, an energetic reaction takes place, with formation of an addition-product, $C_5H_5N \cdot CH_3I$. When warmed with solid potash, this compound gives off a very pungent and disagreeable odour.

450. Many methods for the synthesis of pyridine and its homologues are known, although but few of them afford insight into its constitution. Among them is the formation of pyridine from quinoline (463) and pentamethylenediamine (162). When pentamethylenediamine hydrochloride is submitted to dry distillation, *piperidine*, or hexahydropyridine, is produced, and can be oxidized to pyridine by heating with sulphuric acid:



Another method of preparing pyridine, which is carried out at low temperatures and, therefore, affords even more trustworthy evidence of its constitution, is from ε-chloroamylamine. When an aqueous solution of this substance is heated on a water-bath for some time, it is transformed into the hydrochloride of piperidine:



$$CH_2{<}\begin{matrix}CH_2{-}CH_2{-}Cl\\ CH_2{-}CH_2{-}NH_2\end{matrix} \rightarrow CH_2{<}\begin{matrix}CH_2{-}CH_2\\ CH_2{-}CH_2\end{matrix}{>}NH \cdot HCl.$$

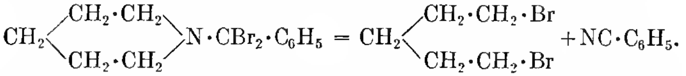
ε-Chloroamylamine

ε-Chloroamylamine was thus obtained by **Gabriel**. γ-Chloropropylphenyl ether, obtained from α-chloro-α′-bromopropane and sodium phenoxide, reacts thus with diethyl monosodiomalonate:

$$C_6H_5O \cdot CH_2 \cdot CH_2 \cdot CH_2Cl + NaCH(COOC_2H_5)_2 =$$
$$= C_6H_5O \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(COOC_2H_5)_2.$$

On saponification of this ester, and subsequent heating of the acid obtained, one molecule of carbon dioxide is eliminated, with formation of δ-phenoxyvaleric acid, $C_6H_5O\cdot(CH_2)_4\cdot COOH$. When this acid is heated with lead thiocyanate, it is converted into the corresponding nitrile, $C_6H_5O\cdot(CH_2)_4\cdot CN$, which is reduced by sodium and alcohol to ε-phenoxyamylamine, $C_6H_5O\cdot(CH_2)_5\cdot NH_2$. On heating with hydrochloric acid, the phenoxyl-group in this amine is replaced by chlorine.

The converse of these syntheses is the decomposition of piperidine, discovered by VON BRAUN. On treatment of *benzoylpiperidine*, $C_5H_{10}N\cdot COC_6H_5$, with phosphorus pentabromide, PBr_5, the oxygen is replaced by two bromine atoms. Distillation converts this dibromo-derivative into *pentamethylene dibromide* and benzonitrile:

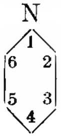


$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right\rangle\mathrm{N\cdot CBr_2\cdot C_6H_5} = \mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CH_2\cdot CH_2\cdot Br}\\ \mathrm{CH_2\cdot CH_2\cdot Br}\end{matrix}\right. + \mathrm{NC\cdot C_6H_5}.$$

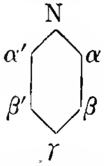
A practical method is thus afforded of preparing pentamethylene dibromide, a substance of importance in various syntheses.

451. Since pyridine is reduced to piperidine by sodium and alcohol, and piperidine can be oxidized to pyridine, it may be assumed that pyridine has the same closed chain as piperidine; that is, one of five C-atoms and one N-atom. Moreover, it can be proved that the N-atom in pyridine is not linked to hydrogen; for, while piperidine possesses the character of a secondary amine, yielding a nitroso-derivative, for example, pyridine has that of a tertiary amine; thus, it yields an addition-product with methyl iodide (449), and the iodine atom in this substance, like that in other ammonium iodides, can be exchanged for hydroxyl by means of moist silver oxide.

The number of isomeric substitution-products, like that of benzene (288), indicates that *each carbon atom is in union with one hydrogen atom.* A substance of the formula



or



should yield three monosubstitution-products, $2(\alpha)=6(\alpha')$, $3(\beta)=5(\beta')$, and $4(\gamma)$. Moreover, for similar substituents, six disubstitution-products are possible: 2:3 = 6:5; 3:4 = 5:4; 2:4 = 6.4; 2:6, 3:5, and 2:5 = 6:3. This view agrees with the results of experiment. The mode of linking of three out of the four valencies of each carbon atom is thus established, and that of two of the three nitrogen valencies: it remains only to determine how the fourth valency of each carbon atom and the third valency of the nitrogen atom are distributed in the molecule.

The marked analogy between benzene and pyridine leads to the assumption of analogous formulæ for both (289). The great stability of pyridine towards energetic chemical reagents proves that it does not possess double linkings. Only the side-chains of both compounds are attacked by oxidizing agents: with sulphuric acid, both yield sulphonic acids, which are converted by fusion with caustic potash into hydroxyl-derivatives, and by heating with potassium cyanide into cyanides. The hydroxyl-derivatives of pyridine have a phenolic character: they yield characteristic colorations with ferric chloride. Pyridine must, therefore, be regarded as benzene with one of its CH-groups replaced by a N-atom.

Notwithstanding these analogies, there are great differences in the behaviour of benzene and pyridine, one being that pyridine does not admit of nitration.

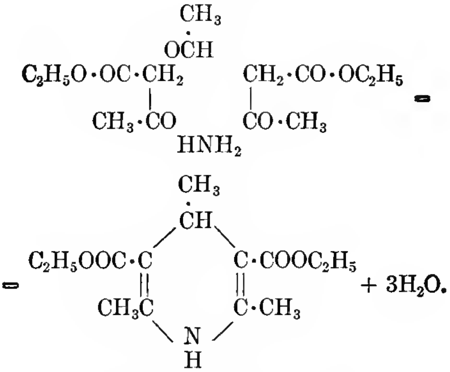
The principle of the orientation of pyridine is the same as that of benzene—conversion of a compound of unknown structure into one with its side-chains in known positions. The monocarboxylic acids and dicarboxylic acids have served as the main basis for its orientation. The method of ascertaining the positions occupied by the carboxyl-groups in these compounds is described in 455.

Homologues of Pyridine.

452. The homologues of pyridine are the *methylpyridines* or *picolines*, *dimethylpyridines* or *lutidines*, and *trimethylpyridines* or *collidines*. Many of them can be obtained by more or less complex methods: thus, β-picoline is formed by the distillation of acroleïn-ammonia (147), and collidine by the distillation of crotonaldehyde-ammonia. The formation of pyridine and its homologues by the dry distillation of bones depends upon these reactions: under the

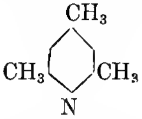
influence of heat, the fat present yields acroleïn, which reacts with the ammonia resulting from the heating of the proteïns, forming pyridine bases.

HANTZSCH has discovered an important synthesis of pyridine derivatives—the condensation of one molecule of aldehyde-ammonia with two molecules of ethyl acetoacetate:



Diethyl dihydrocollidinedicarboxylate

On oxidation with nitrous acid, this substance loses two H-atoms, one from the CH-group and one from the NH-group, with formation of *ethyl collidinedicarboxylate.* On saponification with caustic potash, and subsequent heating of the potassium salt with quicklime, the carboxyl-groups are eliminated, and collidine,



distils.

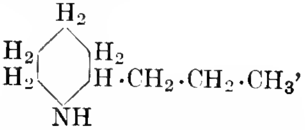
In this synthesis acetaldehyde may be replaced by other aldehydes, and ethyl acetoacetate by the esters of other β-ketonic acids, so that it affords a method of preparing numerous pyridine derivatives.

453. Some of the homologues of pyridine can be obtained from it by the action of an alkyl iodide, an addition-product being formed. On heating this compound to 300°, the alkyl-group becomes detached from the nitrogen atom and linked to a carbon atom, a reaction analogous to the formation of *p*-toluidine by heating methyl aniline hydrochloride to a high temperature (316).

α-Allylpyridine is of theoretical importance. LADENBURG obtained it by the condensation of α-picoline with acetaldehyde:

$$\underset{\alpha\text{-Picoline}}{NC_5H_4\cdot CH_3} + \underset{\text{Acetaldehyde}}{OCH\cdot CH_3} = \underset{\alpha\text{-Allylpyridine}}{NC_5H_4\cdot CH:CH\cdot CH_3} + H_2O.$$

By its aid he effected the first synthesis of a natural alkaloid, that of coniïne, $C_8H_{17}N$ (**473**). α-Allylpyridine was reduced with sodium and boiling alcohol, yielding *α-propylpiperidine*,



optically inactive, like all synthetical substances prepared from inactive material. This substance was resolved into a dextro-rotatory and a lævo-rotatory modification by fractional crystallization of its tartrate, the dextro-rotatory isomeride being named *isoconiïne* because heating at 300° transforms it into an isomeride identical with natural coniïne. LADENBURG attributes the difference between coniïne and *iso*coniïne to asymmetry of the nitrogen atom.

The constitutional formula of α-propylpiperidine indicates that the carbon atom in union with the propyl-group is asymmetric. γ-Propylpiperidine does not contain an asymmetric carbon atom, and should therefore be optically inactive. The side-chain cannot be at the β-position, for coniïne yields ammonia and normal octane when strongly heated with hydriodic acid. Thus treated, a β-propylpiperidine or γ-propylpiperidine must yield an octane with a branched carbon-chain, which proves that coniïne is an α-compound.

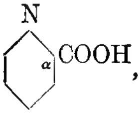
454. *Piperidine* is present in pepper in combination as *piperine*, $C_{17}H_{19}O_3N$. On boiling with alkalis, it yelds *piperic acid*, $C_{12}H_{10}O_4$, and piperidine, by addition of one molecule of water. Piperine must, therefore, be a substituted amide of piperic acid, containing the piperidine-residue, $C_5H_{10}N$—, instead of the NH_2-group:

$$C_5H_{10}N—C_{12}H_9O_3.$$

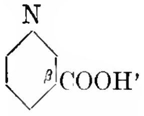
Piperidine is a colourless liquid, boiling at 106°, with a characteristic pepper-like odour and strongly-marked basic properties (**162**). It is best obtained by the electro-reduction of pyridine.

Pyridinecarboxylic Acids.

455. Three *pyridinemonocarboxylic acids* are known.



Picolinic acid (α)



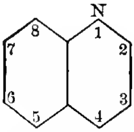
Nicotinic acid (β)

and

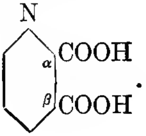
*iso*Nicotinic acid (γ)

The orientation of the carboxyl-groups in these acids can be carried out as follows. It is stated in **453** that the side-chain in coniïne occupies the α-position. On oxidation, this substance yields picolinic acid, by conversion of the propyl-group into a carboxyl-group, and elimination of the six added hydrogen atoms. Picolinic acid is therefore the α-carboxylic acid.

Nicotinic acid is proved to have the β-constitution thus. Quinoline (**463**) has the formula



It is naphthalene with one of the α-CH-groups replaced by N. On oxidation, quinoline yields a pyridinedicarboxylic acid, *quinolinic acid*, which must therefore have the structure



On heating this acid, one molecule of carbon dioxide is eliminated, with formation of nicotinic acid. Since the carboxyl-group in picolinic acid has been proved to occupy the α-position, nicotinic acid must be the β-acid. There remains only the γ-structure for *iso*nicotinic acid.

The pyridinemonocarboxylic acids are formed by the oxidation of the homologues of pyridine containing a side-chain. Nicotinic acid derives its name from its formation by the oxidation of nicotine. The monocarboxylic acids are crystalline, and possess both a basic and an acidic character. As bases, they yield salts with acids, and double salts with platinum chloride and mercuric chloride, etc. As acids, they form salts with bases, the copper salts being often employed in their separation.

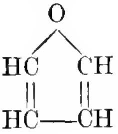
Picolinic acid can be distinguished from its isomerides by two properties: on heating, it loses CO_2 more readily, with formation of pyridine; and it gives a yellowish-red coloration with ferrous sulphate. Quinolinic acid answers to the same tests: it may, therefore, be concluded that they are applicable to acids with a carboxyl-group in the α-position.

456. Pyridine may be regarded as derived from benzene by replacement of one CH-group by N. Other closed-chain compounds are known, derived from benzene by replacement of two CH-groups by O, NH, or S, respectively. Such are *furan* (or *furfuran*), C_4H_4O; *pyrrole*, C_4H_5N; and *thiophen*, C_4H_4S.

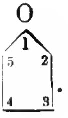
II. FURAN,* C_4H_4O.

457. *Furan*, C_4H_4O, B.P. 36°, is of little importance, but two of its substitution-products must be considered in some detail.

To furan is assigned the ring-formula



or



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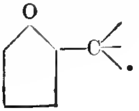
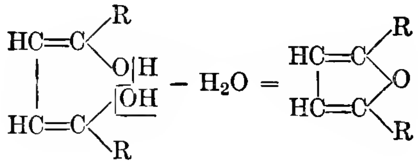
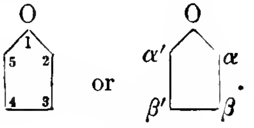
* The CHEMICAL SOCIETY OF LONDON adopts the name *furan* for the simple ring , the corresponding radical being *furyl*. The double syllable *furfur* . . . is reserved for derivatives with a side-chain, containing the ring 

This formula is supported by the resemblance in properties between some of its derivatives, such as *furfuraldehyde* (*furfural* or *furfurole*), $C_4H_3O\cdot C^{H}_{O}$, and the corresponding benzene derivatives. Moreover, the O-atom can be proved to be linked similarly to that of ethylene oxide (156), for on treatment with sodium, furan does not evolve hydrogen, proving the absence of a hydroxyl-group; and it does not react with hydroxylamine or phenylhydrazine, indicating that it has no carbonyl-group.

Furan derivatives can be obtained from the 1:4-diketones, $R\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot R$, by treatment with dehydrating agents, such as acetyl chloride. This reaction may be regarded as the result of the conversion of the diketone into an unstable, tautomeric form, $R\cdot\underset{OH}{C}:CH\cdot CH:\underset{OH}{C}\cdot R$, which loses water:



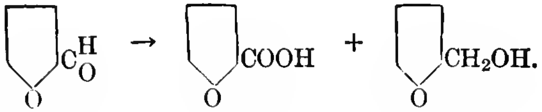
This method yields 2:5-furan derivatives, the C-atoms in furan being denoted as in the scheme



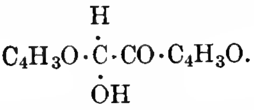
This synthesis of furan derivatives is likewise a proof of their constitution.

458. The most important derivatives of furan are *furfuraldehyde* $C_4H_3O\cdot C^{H}_{O}$, and *pyromucic acid*, $C_4H_3O\cdot COOH$: both have long been known.

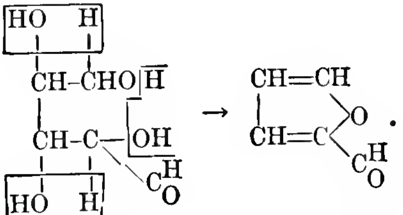
Furfuraldehyde is prepared from pentoses by the method mentioned in **208**. It has the character of an aromatic aldehyde: like benzaldehyde (**335**), it is converted by alcoholic potash into the corresponding acid, pyromucic acid, and the corresponding alcohol, *furfuryl alcohol*, $C_4H_3O\cdot CH_2OH$:



Furfuraldehyde Pyromucic acid Furfuryl alcohol

With ammonia it yields *furfuramide*, $(C_5H_4O)_3N_2$, analogous in composition to hydrobenzamide (335). Just as benzaldehyde condenses in presence of potassium cyanide to benzoïn (428), furfuraldehyde under the same conditions yields the similarly constituted *furfuroïn*,  $C_4H_3O\cdot\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}\cdot CO\cdot C_4H_3O$. The resemblance in properties between the two compounds is, therefore, very striking.

Furfuraldehyde is proved to have the 2-structure by various means: for example, by its formation from pentoses (208), a reaction which may be represented by the scheme:

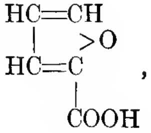


Pentose Furfuraldehyde

Furfuraldehyde thus results from the elimination of three molecules of water under the influence of hydrochloric acid or sulphuric acid. It is a colourless, oily liquid of agreeable odour, and boils at 162°. A test for it is described in 208.

As its name indicates, pyromucic acid is formed by the dry distillation of mucic acid (209, 4). It can also be obtained by oxidizing furfuraldehyde with silver oxide. It is crystalline, melts at 132°, can be readily sublimed, and dissolves freely in hot water. When heated at 275° in a sealed tube, it yields carbon dioxide and furan.

Pyromucic acid wholly lacks the character of an aromatic compound: its properties in no way resemble those of benzoïc acid, but are like those of the unsaturated aliphatic acids. Thus, it easily undergoes oxidation: it almost instantaneously decolorizes von Baeyer's reagent (123), and readily adds four bromine atoms. Hence, the distinguishing characteristics of the benzene-nucleus are absent, so that the formula



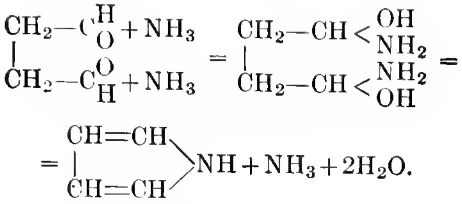
with two double bonds, must be assigned to it.

III. PYRROLE, C_4H_5N.

459. Pyrrole is the most important of the heterocyclic compounds with a ring of five atoms. Several natural products containing the pyrrole-nucleus are known: examples are the colouring-matter of blood; chlorophyll; and certain alkaloids, among them nicotine. Pyrrole derivatives have also been found among the decomposition-products of proteïns. Pyrrole is a constituent of "Dippel's oil" (449). The fraction of this oil which distils between 120° and 130° is employed in the preparation of pyrrole. After removal of the pyridine bases by treatment with dilute sulphuric acid, and of the nitriles by boiling with sodium carbonate, the fraction is dried, and treated with potassium. *Potassiopyrrole*, C_4H_4NK, is formed, and can be purified by washing with ether. It is reconverted into pyrrole by the action of water.

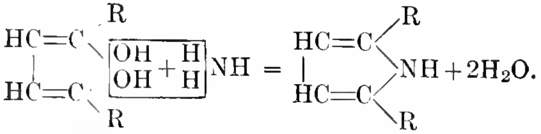
Pyrrole is a colourless liquid, specifically somewhat lighter than water, and boiling at 131° On exposure to light, it soon acquires a brown colour. The vapours of pyrrole and its derivatives impart a carmine-red colour to a wood-shaving moistened with hydrochloric acid, due to the formation of an amorphous substance. "pyrrole-red." This reaction furnishes a delicate test for pyrrole and its derivatives.

Pyrrole can be synthesized by several methods: for example, by the interaction of succindialdehyde and ammonia:



Pyrrole

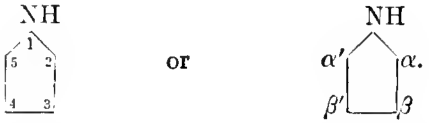
Its homologues can be obtained by the action of ammonia upon 1:4-diketones:



1:4-Diketone (tautomeric form)

αα'-Pyrrole

The nomenclature of the pyrrole derivatives is indicated in the scheme



This structure is inferred from the foregoing syntheses and otherwise. The basic properties which should be characteristic of a substance with the formula of pyrrole are masked by the resinifying action of acids. As a result of this influence, no sulpho-acids have been obtained, and nitro-derivatives only by an indirect method.

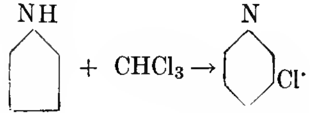
Among the properties of pyrrole indicating its relation to the aromatic compounds is its behaviour with halogens: unlike an aliphatic unsaturated compound, it yields substitution-products, but not addition-products. The analogy in properties between pyrrole and aniline, and especially phenol, is very marked. The transformation of 1-*methylpyrrole* into 2-*methylpyrrole* under the influcnce of heat resembles the conversion of methylaniline into *p*-toluidine (316):

$$\underset{\text{1-Methylpyrrole}}{C_4H_4N\cdot CH_3} \rightarrow \underset{\text{2-Methylpyrrole}}{C_4H_3(CH_3)\cdot NH.}$$

Just as sodium phenoxide is converted by carbon dioxide into salicylic acid (386), so potassiopyrrole and carbon dioxide yield

2-pyrrolecarboxylic acid. Like phenol, pyrrole unites with benzenediazonium chloride, with elimination of hydrochloric acid (343).

When pyrrole is treated with chloroform in presence of sodium alkoxide, a notable reaction ensues. The C-atom of the chloroform takes up a position between two of the C-atoms of the pyrrole-nucleus, forming *β-chloropyridine:*



Pyrrole β-Chloropyridine

On reduction with zinc-dust and cold hydrochloric acid, pyrrole takes up two hydrogen atoms, forming *dihydropyrrole,** C_4H_7N, which boils at 91°. Like the partial reduction-products of aromatic compounds, dihydropyrrole behaves as an unsaturated compound, another indication of the aromatic character of pyrrole.

IV. THIOPHEN, C_4H_4S.

460. *Thiophen* has the most aromatic character of the compounds mentioned in 456.

It is present in the crude benzene obtained from coal-tar (293) to the extent of about 0·5 per cent.: its homologues, *thiotolen* or methylthiophen, and *thioxen* or dimethylthiophen, are contained in toluene and xylene from the same source.

Thiophen was first obtained by Victor Meyer by agitating coal-tar benzene with small amounts of concentrated sulphuric acid till it ceased to give the *indophenin-reaction,* a blue coloration with isatin (466) and concentrated sulphuric acid. By this treatment the thiophen is converted into a sulphonic acid, from which it can be regenerated by the action of superheated steam.

A better method for the separation of benzene and thiophen is to boil the crude benzene with mercuric oxide and acetic acid. The thiophen is precipitated as *thiophen mercury oxyacetate,* $C_4H_2S(HgOOC\cdot CH_3)\cdot HgOH$, which is reconverted into thiophen by distillation with moderately concentrated hydrochloric acid.

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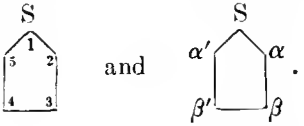
* The Chemical Society of London employs the name *dihydropyrrole* for the compound C_4H_7N, and *tetrahydropyrrole* for C_4H_9N. In the nomenclature of the German Chemical Society the corresponding terms are *pyrrolin* and *pyrrolidin*

Thiophen can be synthesized by various methods, the most important being the interaction of succinic acid and phosphorus pentasulphide. On heating a mixture of these substances, a vigorous reaction ensues, carbon disulphide is evolved, and a liquid, consisting chiefly of thiophen, distils.

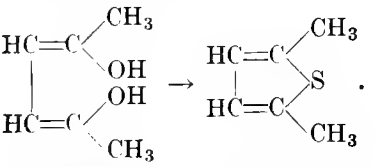
It is a colourless liquid, boiling at 84°, a temperature which differs little from the boiling-point of benzene (80·4°). It has a faint, non-characteristic odour. It is heavier than water, its specific gravity being 1·062 at 23°.

Bromine reacts energetically with thiophen, forming chiefly *dibromothiophen*, $C_4H_2Br_2S$, along with a small proportion of the monobromo-derivative.

The notation of thiophen derivatives is indicated by the schemes

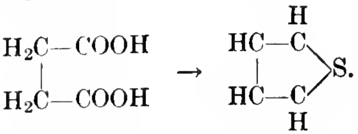


The homologues of thiophen can be obtained by FITTIG'S synthesis (294) and by other methods: for instance, by heating 1:4-diketones with phosphorus pentasulphide, a mode of synthesis which proves the constitution of the thiophen homologues. Thus, acetonylacetone yields *dimethylthiophen*:



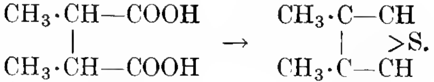
Acetonylacetone (tautomeric form) 2:5-Dimethylthiophen

2:5-Dialkylthiophens are obtained from 1:4-diketones: the 3:4-alkyl-compounds can be prepared by another method. As stated, thiophen results from the interaction of succinic acid and phosphorus pentasulphide:



Succinic acid Thiophen

Similarly, a monoalkylsuccinic and symmetrical dialkylsuccinic acid respectively yield a 3-alkylthiophen and a 3:4-alkylthiophen:

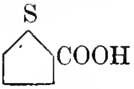


$$\begin{array}{l}CH_3{\cdot}CH{-}COOH\\ \quad\;|\\ CH_3{\cdot}CH{-}COOH\end{array} \longrightarrow \begin{array}{l}CH_3{\cdot}C{-}CH\\ \qquad |\quad >S.\\ CH_3{\cdot}C{-}CH\end{array}$$

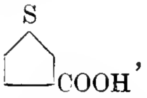
Symmetrical dimethylsuccinic acid 3:4-Dimethylthiophen

The known structure of these compounds can be employed as a basis for the orientation of the derivatives of thiophen.

When a cold aqueous solution of the two monocarboxylic acids, *2-thiophencarboxylic acid* and *3-thiophencarboxylic acid,*



and



,

is crystallized slowly, there is formed a mixture which cannot be resolved into its components. This phenomenon is due to the formation of mixed crystals, and is of rare occurrence with position-isomerides. On oxidizing a mixture of 2-thiotolen and 3-thiotolen, an apparently homogeneous acid is obtained: from its method of formation, however, it can only be a mixture of the corresponding acids.

Thiophenketones are prepared by Friedel and Crafts's reaction (294): thus, acetothiënone or *2-thiënylmethylketone,* $C_4H_4S{\cdot}COCH_3$, is obtained from acetyl chloride, thiophen, and aluminium chloride. These ketones are readily oxidized to thiophencarboxylic acids, a good method of preparing these compounds.

A *thiophensulphonic acid* is also known: it is more easily formed than benzenesulphonic acid, which is the basis of Victor Meyer's method of separating thiophen and benzene. On distillation with potassium cyanide, it forms the corresponding nitrile; but the sulpho-group is not exchanged for hydroxyl by fusion with caustic potash. It is possible, however, to obtain a *thiophenphenol* by the interaction of aminothiophen hydrochloride and nitrous acid, which yields a nitrated hydroxyl-derivative, $C_4H_2S{<}\substack{NO_2\\ OH}$. This compound greatly resembles *p*-nitrophenol; thus, it dissolves in alkalis, yielding a solution of yellow colour.

On volatilizing thiophen in a current of air, and passing the resulting gaseous mixture into carefully cooled, fuming nitric acid, the principal product is *dinitrothiophen*, although *mononitrothiophen* is also formed. The mononitro-compound is a solid, melting at 44°, and boiling at 224°: it has an odour like that of nitrobenzene. On reduction, it yields *amidothiophen*, or *thiophenine*, which differs from aniline in being very unstable: it changes quickly to a varnish-like mass, but its hydrochloride is stable. It does not yield diazo-compounds, but reacts with benzenediazonium chloride, forming a crystalline, orange dye.

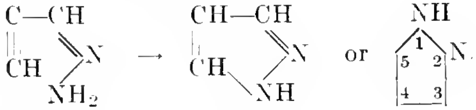
Many other thiophen derivatives have been obtained, chiefly through the researches of VICTOR MEYER. The examples cited suffice to indicate the great analogy subsisting between the properties of thiophen and those of benzene.

V. PYRAZOLE, $C_3H_4N_2$.

461. *Pyrazole* is formed in several reactions, one of them being the combination of hydrazine with propiolaldehydeacetal (**148**):

$$\underset{\text{Propiolaldehydeacetal}}{CH \equiv C \cdot CH(OC_2H_5)_2} + H_2N \cdot NH_2 =$$

$$= \underset{\substack{\text{Intermediate product} \\ \text{(not isolated)}}}{CH \equiv C \cdot CH = N \cdot NH_2} + 2C_2H_5OH;$$

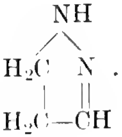


Intermediate product Pyrazole

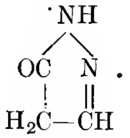
This synthesis proves that pyrazole has the formula indicated, so that it may be regarded as pyrrole in which one of the CH-groups has been replaced by N.

It is crystalline, melts at 70°, and is very stable. It is only a weak base, for its aqueous solution has a neutral reaction.

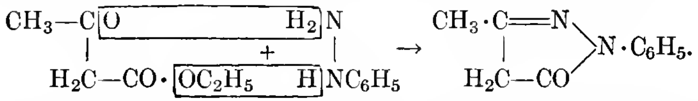
Pyrazole itself does not yield important derivatives, but such are obtained from a dihydride, *pyrazoline*, $C_3H_6N_2$, formed by the action of hydrazine hydrate on acroleïn. This substance has the formula



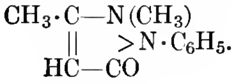
Bromine converts it into pyrazole. A ketonic derivative of pyrazoline, called *pyrazolone*, has the formula



Substitution-products of it are obtained by the interaction of ethyl acetoacetate and phenylhydrazine:



Methylphenylpyrazolone is thus formed. Methylphenylhydrazine, $C_6H_5 \cdot NH \cdot NH \cdot CH_3$, condenses similarly with ethyl acetoacetate, yielding a dimethylphenylpyrazolone of the formula



This is *antipyrine*, $C_{11}H_{12}ON_2$, discovered by KNORR, and extensively employed in medicine as a febrifuge. It crystallizes in white leaflets melting at 113°. It cannot be distilled without undergoing decomposition. It is readily soluble in water and alcohol: the aqueous solution gives a red coloration with ferric chloride, and a bluish-green coloration with nitrous acid.

Many other ring-compounds are known, containing rings of six, as well as of five atoms, but they are beyond the scope of this book.

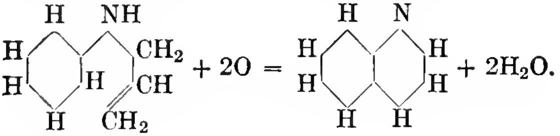
CONDENSATION-PRODUCTS OF BENZENE AND HETEROCYCLIC NUCLEI.

462. Only three of the condensation-products of benzene and heterocyclic nuclei will be described: *quinoline*, iso*quinoline*, and *indole*. The first two are related to the alkaloids, and the last is important on account of its connection with indigo.

I. QUINOLINE, C_9H_7N.

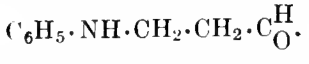
463. Quinoline is present in coal-tar and bone-oil, but is difficult to obtain pure from these sources. It is usually prepared by SKRAUP's synthesis, described below. It is a colourless, highly refractive liquid of characteristic odour: it boils at 236°, and has a specific gravity of 1·1081 at 0° It has the character of a tertiary base, so that it possesses no hydrogen linked to nitrogen. It yields salts with acids: the dichromate, $(C_9H_7N)_2H_2Cr_2O_7$, dissolves with difficulty in water.

Quinoline can be synthesized by various methods which prove its constitution. Its synthesis was first effected by KÖNIGS, by passing allylaniline-vapour over red-hot oxide of lead:



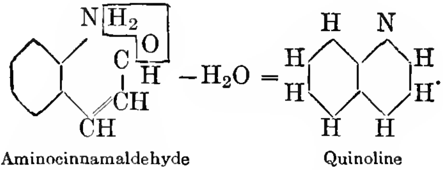
Allylaniline

SKRAUP's synthesis consists in heating together aniline, glycerol, sulphuric acid, and nitrobenzene. In presence of sulphuric acid as a dehydrating agent, the glycerol loses water, forming acroleïn, which unites with the aniline to an addition-product,


$$C_6H_5\cdot NH\cdot CH_2\cdot CH_2\cdot C{\genfrac{}{}{0pt}{}{H}{O}}.$$

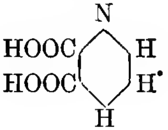
In KÖNIG's synthesis the oxidizing agent is the lead oxide; in this reaction it is the nitrobenzene, which is reduced to aniline. Arsenic acid can be substituted for nitrobenzene.

Von Baeyer and Drewsen have discovered another method of synthesis which proves the constitution of quinoline: it involves the reduction of *o*-nitrocinnamaldehyde. This compound is first converted into an intermediate product, the corresponding amino-derivative, the H-atoms of the NH_2-group of this substance being subsequently eliminated along with the O-atom of the aldehyde-group:



o-Aminocinnamaldehyde Quinoline

The last synthesis proves quinoline to be an *ortho*-substituted benzene: the constitution of the ring containing the N-atom has now to be determined. The method employed is based upon oxidation, which produces a dibasic acid, *quinolinic acid*,



On distillation with quicklime, quinolinic acid yields pyridine. From these facts it must be concluded that quinoline contains a benzene-nucleus and a pyridine-nucleus, with two *ortho*-C-atoms common to both. It may be regarded as naphthalene, with one of the CH-groups, 1-4-5-8, replaced by N.

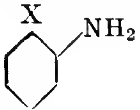
The number of isomeric substitution-products is very large. The seven hydrogen atoms occupy dissimilar positions relative to the nitrogen atom, and consequently seven monosubstitution-products are possible. Twenty-one disubstitution-products are possible for similar substituents, while the number of tri-derivatives possible is much greater, and so on.

464. There are three methods for the orientation of quinoline derivatives.

First, the relative method (**398**, 1).

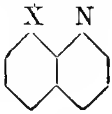
Second, oxidation. This usually removes the benzene-nucleus, leaving the pyridine-nucleus intact, and thus furnishes a means of determining which substituents are present in each.

Third, Skraup's synthesis—an important aid to orientation. It can be carried out not only with aniline, but with many of its substitution-products, such as homologues of aniline, nitroanilines, aminophenols, and other derivatives. The quinoline compounds thus obtained have their substituents in the benzene-nucleus. But this synthesis also indicates the positions of the side-chains when an *ortho*-substituted or a *para*-substituted aniline is used: thus,



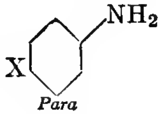
Ortho

can only yield



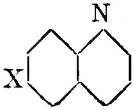
,

and



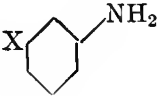
Para

only



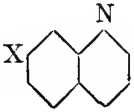
;

while

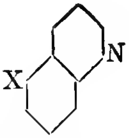


Meta

can yield



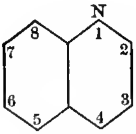
or



.

All four possible quinoline derivatives with substituents in the benzene-nucleus can, therefore, be prepared by Skraup's synthesis.

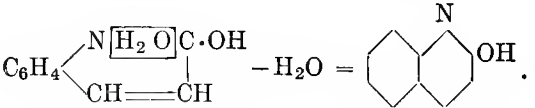
The nomenclature of the quinoline derivatives is indicated in the scheme



Many of the known quinoline derivatives are obtained by Skraup's method, a smaller number directly from quinoline. The sulphonic acids are best prepared by the latter method. On fusion with caustic potash, they are converted into hydroxyquinolines;

when heated with potassium cyanide, they yield cyanoquinolines, which on hydrolysis give carboxylic acids.

Carbostyril, or 2-hydroxyquinoline, can be synthesized by the elimination of water from *o*-aminocinnamic acid:



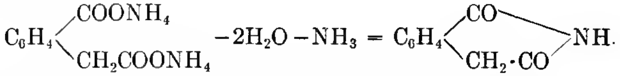
o-Aminocinnamic acid Carbostyril

It has a phenolic character: thus, it dissolves in alkalis, and is reprecipitated by carbon dioxide.

II. *iso*QUINOLINE, C_9H_7N.

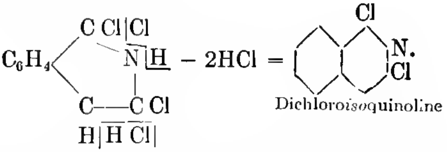
465. iso*Quinoline* is present in coal-tar, from which **Hoogewerff** and **van Dorp** isolated it in the form of its sparingly soluble sulphate. It is a colourless substance with an odour like that of quinoline. It melts at 21°, and boils at 237°.

Its synthesis indicates its constitution. On heating, the ammonium salt of *homophthalic acid*, $C_6H_4<\begin{matrix}COOH & 1\\ CH_2\cdot COOH & 2\end{matrix}$, is converted into *homophthalimide:*



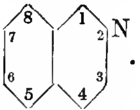
$$C_6H_4\begin{matrix}\diagup COONH_4\\ \diagdown CH_2COONH_4\end{matrix} - 2H_2O - NH_3 = C_6H_4\begin{matrix}\diagup CO\\ \diagdown CH_2\cdot CO\end{matrix}>NH.$$

On treating with phosphorus oxychloride, each O-atom is replaced by two Cl-atoms, 2HCl being subsequently eliminated, with formation of *dichloro*iso*quinoline:*



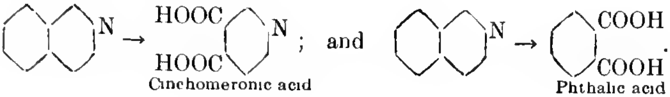
Dichloro*iso*quinoline

Reduction with hydriodic acid and phosphorus converts this substance into *iso*quinoline, in which the N-atom of the pyridine-nucleus is not directly linked to the benzene-nucleus, wherein it differs from ordinary quinoline:



*iso*Quinoline

The products obtained by the oxidation of *iso*quinoline support this view of its constitution. The benzene-ring is removed from one part, and the pyridine-ring from the other, so that cinchomeronic acid and phthalic acid are formed:

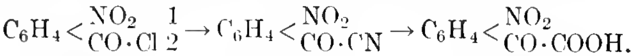


Cinchomeronic acid Phthalic acid

III. INDOLE, C_8H_7N.

466. The relation between indigo and *indole*, mentioned in **462**, is made evident by the following series of transformations, chiefly the discoveries of VON BAEYER.

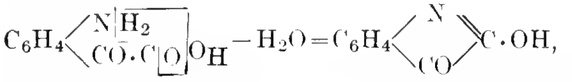
On treatment with nitric acid, indigo, $C_{16}H_{10}O_2N_2$, yields an oxidation-product, *isatin*, $C_8H_5O_2N$, which can also be synthesized by treating *o*-nitrobenzoyl chloride with silver cyanide. When hydrolyzed, the resulting nitrile yields *o*-nitrobenzoylformic acid:



$$C_6H_4{<}\begin{matrix}NO_2\\CO\cdot Cl\end{matrix}\ \begin{matrix}1\\2\end{matrix}\rightarrow C_6H_4{<}\begin{matrix}NO_2\\CO\cdot CN\end{matrix}\rightarrow C_6H_4{<}\begin{matrix}NO_2\\CO\cdot COOH.\end{matrix}$$

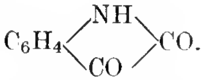
o-Nitrobenzoyl chloride *o*-Nitrobenzoyl cyanide *o*-Nitrobenzoylformic acid

On reduction, the nitro-group in this acid is converted into an amino-group, and water eliminated simultaneously with the formation of isatin, which has, therefore, the constitution indicated by the equation



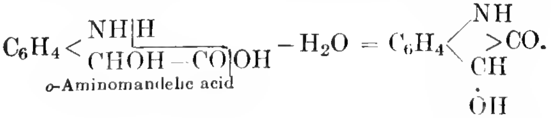
$$C_6H_4{<}\begin{matrix}N\boxed{H_2}\\CO\cdot C\boxed{O}OH\end{matrix} - H_2O = C_6H_4{<}\begin{matrix}N\\CO\end{matrix}{>}C\cdot OH,$$

o-Aminobenzoylformic acid Isatin or



$$C_6H_4{<}\begin{matrix}NH\\CO\end{matrix}{>}CO.$$

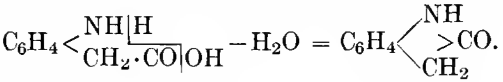
When reduced with zinc-dust and hydrochloric acid, isatin takes up two hydrogen atoms, forming *dioxindole*, $C_8H_7O_2N$. This compound also results on the elimination of water from the unstable *o*-aminomandelic acid, which determines its constitution:



$$C_6H_4{<}\begin{matrix}NH\boxed{H}\\CHOH-CO\boxed{OH}\end{matrix} - H_2O = C_6H_4{<}\begin{matrix}NH\\ \underset{OH}{CH}\end{matrix}{>}CO.$$

o-Aminomandelic acid Dioxindole

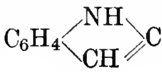
When reduced with tin and hydrochloric acid, dioxindole yields *oxindole*, C_8H_7ON, which is also obtained by reduction of *o*-nitrophenylacetic acid and subsequent elimination of water:



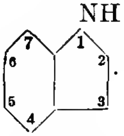
$$C_6H_4<\begin{matrix}NH|H\\ CH_2\cdot CO|OH\end{matrix} - H_2O = C_6H_4\begin{matrix}\diagup NH\\ \quad >CO.\\ \diagdown CH_2\end{matrix}$$

o-Aminophenylacetic acid Oxindole

Distillation with zinc-dust converts oxindole into *indole*, C_8H_7N, which must, therefore, have the structure



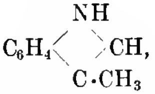
$C_6H_4\begin{matrix}\diagup NH \diagdown\\ \qquad >CH;\\ \diagdown CH \diagup\end{matrix}$ or



Indole

Indole, therefore, possesses a benzene-nucleus condensed with a pyrrole-nucleus. It does, in fact, display some of the properties characteristic of pyrrole: thus, it is a very weak base, and gives a red coloration with hydrochloric acid.

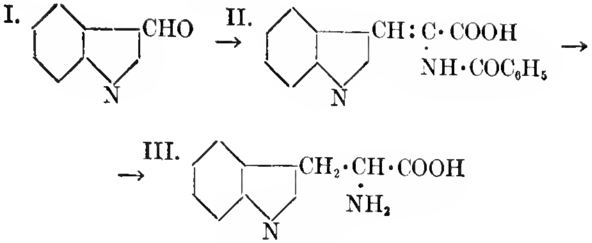
467. 3-*Methylindole*, or *skatole*,



$$C_6H_4\begin{matrix}\diagup NH \diagdown\\ \qquad >CH,\\ \diagdown C\cdot CH_3 \diagup\end{matrix}$$

is present in fæces, and occasions the unpleasant odour. It is also found in a species of wood grown in India, and is formed in the putrefactive decay of proteïns, or by fusing proteïns with caustic potash.

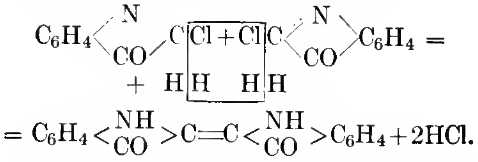
Tryptophan, $C_{11}H_{12}O_2N_2$, is an important decomposition-product of albumin (243) and an indole derivative. It is synthesized by treating indole with chloroform and potassium hydroxide in alcoholic solution. *β-Indolealdehyde* (I.) is formed as an intermediate product, and condenses with hippuric acid to *indolylbenzoylaminoacrylic acid* (II.). On treatment with sodium and alcohol, the double bond of this compound adds two hydrogen atoms and the benzoyl-group is simultaneously eliminated, with formation of racemic tryptophan (III.):



Tryptophan

Indigo.

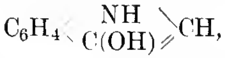
468. The constitution of indigo is inferred from its formation from *isatin chloride*, obtained by the interaction of isatin and phosphorus pentachloride. On reduction with zinc-dust and acetic acid, it is transformed into indigo:



$$\begin{array}{l} C_6H_4\genfrac{<}{>}{0pt}{}{N}{CO}C\,\boxed{\begin{matrix}Cl+Cl\\ H\quad H\end{matrix}}\,C\genfrac{<}{>}{0pt}{}{N}{CO}C_6H_4 = \\ \qquad + H \qquad\qquad\qquad H \\ = C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}>C{=}C<\genfrac{}{}{0pt}{}{NH}{CO}>C_6H_4+2HCl. \end{array}$$

Since on treatment with sulphuric acid, and subsequent reduction, o-*dinitrodiphenyldiacetylene*, $\begin{matrix}C_6H_4\cdot C{\equiv}C{-}C{\equiv}C\cdot C_6H_4\\ NO_2 \qquad\qquad\qquad\qquad NO_2\end{matrix}$, is converted into indigo, the two isatin-residues in the latter must be united by a carbon linking.

469. Indigo has long been known as one of the most beautiful blue dyes, and is very permanent, being unaffected by light, acids, alkalis, or washing. It is prepared from certain plants, among them *Indigofera tinctoria* and *leptostycha*. They are cultivated on a large scale in Bengal in India—whence the dye derives its name—as well as in Central America, Java, and other countries. Indigo is not present in the plant as such, but in combination as the glucoside *indican*, which is present chiefly in the leaves, and can be extracted with hot water. It is crystalline, and has the formula $C_{14}H_{17}O_6N+3H_2O$. In addition to the glucoside, the leaves contain an enzyme, the activity of which, like that of all enzymes, is destroyed by boiling water: hence, when indican itself is to be prepared, hot water must be employed in the extraction. With cold water, both indican and the unchanged enzyme dissolve, and the glucoside decomposes into dextrose and *indoxyl*, C_8H_7ON, or



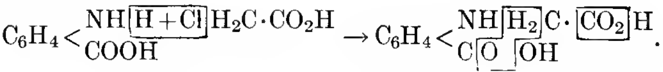
$$C_6H_4\left\langle\begin{matrix}NH\\C(OH)\end{matrix}\right\rangle CH,$$

a substance which is moderately stable in acid solution, but in dilute alkaline solution is quickly oxidized to indigo by atmospheric oxygen.

The manufacture of indigo from the plants containing it is carried out by the method indicated. The leaves of the indigo-plant are allowed to remain immersed in lukewarm water for some hours: the aqueous extract is "churned" by a revolving water-wheel with wooden paddles, which aerates it, and thus oxidizes the indoxyl to indigo. The oxidation-process is facilitated by the addition of slaked lime to make the liquid faintly alkaline. The indigo formed sinks to the bottom, is removed by filtration, and dried. It is put on the market in the form of small cubes.

In addition to the blue dye, *indigotin*, commercial indigo contains indiglucin, indigo-brown, and indirubin; these substances can be extracted by water, alcohol, and alkalis, in which indigotin is insoluble. Indigotin is a dark-blue powder, which, when rubbed, has a copper-like lustre. It can be sublimed *in vacuo*, so that it is possible to determine its vapour-density. It is insoluble in most solvents, but can be crystallized from nitrobenzene or aniline. It dissolves in fuming sulphuric acid, with formation of sulphonic acids.

On account of the great industrial importance of indigo, many attempts have been made to synthesize it. One method is commercially successful, enabling the artificial product to be sold at the same price as natural indigo. It yields pure indigotin, which is sometimes an advantage. This method is employed by the BADISCHE ANILIN- UND SODA-FABRIK of Ludwigshafen-on-Rhine. Anthranilic acid, or *o*-aminobenzoïc acid (397), $C_6H_4<\begin{matrix}NH_2\\COOH\end{matrix}$, combines with monochloroacetic acid to form *phenylglycine*-o-*carboxylic acid:*



$$C_6H_4<\begin{matrix}NH\boxed{H+Cl}H_2C\cdot CO_2H\\COOH\end{matrix}\rightarrow C_6H_4<\begin{matrix}NH\boxed{H_2}C\cdot\boxed{CO_2}H\\C\boxed{O\ \ OH}\end{matrix}.$$

Phenylglycine-*o*-carboxylic acid

Fusion with caustic soda transforms this compound into indoxyl,  $C_6H_4\begin{matrix}NH\\C(OH)\end{matrix}\diagdown CH$, which in alkaline solution is converted by atmospheric oxidation into indigo.

The manufacture of indigo by this method has been rendered possible by the discovery of a satisfactory process for the manufacture of anthranilic acid. It is obtained by oxidizing naphthalene to phthalic acid (367), which can be converted into anthranilic acid, with intermediate production of phthalimide (397).

On reduction, indigo takes up two hydrogen atoms, with formation of *indigo-white*, $C_{16}H_{12}O_2N_2$, a white, crystalline substance, the phenolic character of which is proved by its solubility in alkalis. In alkaline solution it is speedily reconverted into indigo by atmospheric oxidation, a reaction employed in dyeing with this substance. The dye is first reduced to indigo-white, and the fabric thoroughly soaked in an alkaline solution of this compound: on exposure to the air, the indigo-blue formed is fixed on the fibres. The process is technically known as "indigo-vat-dyeing."

The reduction of indigo to indigo-white is variously carried out in the dyeing-industry according to whether wool, silk, or cotton is to be dyed. Reduction is best effected with a salt of hyposulphurous acid, $H_2S_2O_4$ ("Inorganic Chemistry," 83), for the two first named. The solution is mixed with zinc hyposulphite, and treated with excess of milk of lime, which precipitates zinc hydroxide. The indigo is mixed with water, and warmed to about 60° with the solution of calcium hyposulphite, a concentrated alkaline solution of indigo-white being obtained in a short time. On adding to it sufficient water in the dyeing-vat, the bath is ready for use.

The hyposulphite reduction-process possesses the advantage that the reduction stops at the formation of indigo-white, so that almost none of the indigo is lost.

ALKALOIDS.

470. Plants of certain families contain substances, usually of complex composition and basic character, called *alkaloids*. Their classification in one group is of old standing, and had its origin in an idea similar to that which prevailed concerning the vegetable acids (1) prior to the determination of their constitution. Just as the latter have been subdivided into different classes, such as monobasic, polybasic, aliphatic, and aromatic acids, so it has become apparent that the individual alkaloids can be arranged in different classes. Most of the alkaloids are related to pyridine, quinoline, or *iso*quinoline, while a smaller number belong to the aliphatic series. Some of the latter class are described along with the compounds of similar chemical character: among them are betaïne (230), muscarine (248), choline (162), caffeïne, and theobromine (278). Only alkaloids which are derivatives of pyridine are described in this chapter: to them the name alkaloids, in its more restricted sense, is applied, the other substances being known as vegetable bases.

PROPERTIES.

471. It is seldom that an alkaloid is present in more than one family of plants: many families do not contain them. The occurrence of alkaloids is almost entirely confined to dicotyledonous plants. Only a few, such as *coniïne* and *nicotine*, are liquids: most of them are crystalline. Many are optically active and lævo-rotatory: it is very exceptional for them to exhibit dextro-rotation. They have an alkaline reaction and a bitter taste: most of them are insoluble in water, more or less soluble in ether, and readily soluble in alcohol. Most are insoluble in alkalis, but dissolve in acids, forming salts which are sometimes well-defined, crystalline substances.

OUDEMANS observed that the specific rotatory power (27, 2) of the alkaloid salts of strong acids in aqueous solution depends only on the alkaloid, and is not influenced by the nature of the acid-radical; while for the salts of weak acids it depends on the nature of both the alkaloid and the acid. This is explained by the theory of electrolytic dissociation: when dissolved, the salts of strong acids are almost completely ionized, so that in solutions of equimolecular concentration there is always the same amount of the optically active cathion present. The salts of weak acids, however, are to a great extent non-ionized, so that they possess a different (smaller) specific rotatory power.

Many alkaloids can be identified by characteristic colour-reactions. Some substances precipitate many of the alkaloids from their aqueous or acid solution: such *general alkaloid-reagents* are tannin (**389**), phosphomolybdic acid, mercuric potassium iodide, $KI \cdot HgI_2$ ("Inorganic Chemistry," **273**), and others. Some alkaloids are excessively poisonous.

Strong tea is sometimes employed as an antidote, the tannin present precipitating the alkaloid, and rendering it innocuous.

Most of the alkaloids are tertiary amines, and consequently yield addition-products with methyl iodide: none of them possesses the character of a primary amine. Many contain acid-residues or methoxyl-groups: the former are removed by saponification, effected by heating with bases or acids, the latter by heating with hydriodic acid, which yields methyl iodide. Hydroxyl-groups can be identified in the ordinary way with acid chlorides or acetic anhydride (**95** and **96**). On dry distillation, or on heating with zinc-dust, substituted pyridines are sometimes formed.

On account of the complex constitution of the alkaloids, the structures of many of them remain undetermined, so that a rational classification is not yet possible.

472. In the extraction of the alkaloids from plants the latter are cut up into fine pieces and lixiviated with acidified water in a conical vat tapering towards the bottom, where there is a layer of some material such as glass-wool or lint. The effect is that the acidified water gradually sinks through a thick layer of the substance under extraction, a process technically known as "percolation." Dyes, carbohydrates, inorganic salts, etc., are dissolved along with the alkaloids. When the alkaloid is volatile with steam, it can be separated by this means from the liquid, after making the mixture alkaline: when it is comparatively insoluble, it can be obtained by filtration. Further purification is always necessary, and is effected by crystallizing the free alkaloid or one of its salts several times.

INDIVIDUAL ALKALOIDS.

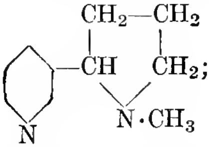
Coniïne, $C_8H_{17}N$.

473. The synthesis of *coniïne* is described in **453**. It is present in spotted hemlock (*Conium maculatum*), and is a colourless liquid of stupefying odour. It boils at 167°, is but slightly soluble in water, and is very poisonous.

Nicotine, $C_{10}H_{14}N_2$.

474. *Nicotine* is present in combination with malic acid and citric acid in the leaves of the tobacco-plant (*Nicotiana tabacum*). It is a colourless, oily liquid, which is lævo-rotatory, and readily soluble in water. It has a tobacco-like odour, which is not so marked in a freshly-distilled sample as in one which has stood for some time. It boils at 246·7°, and is excessively poisonous. It quickly turns brown on exposure to air. It is a ditertiary base: on oxidation with potassium permanganate, it is converted into nicotinic acid (**455**), proving it to be a β-derivative of pyridine.

The constitutional formula of nicotine is

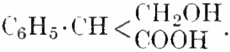


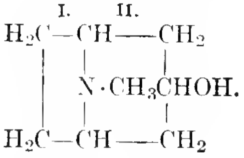
with a hydrogenated pyrrole-nucleus methylated at the nitrogen atom, and a β-substituted pyridine-nucleus. The formula also expresses the facts that nicotine is a ditertiary basis and that it yields nicotinic acid on oxidation. This formula is proved by the synthesis of nicotine; which yields an optically inactive modification resolvable into components. The lævo-rotatory isomeride is identical with natural nicotine. The dextro-rotatory form is much less poisonous than the lævo-rotatory, and also differs from it in other respects in its physiological action.

Atropine, $C_{17}H_{23}O_3N$.

475. *Atropine* is present in the berry of the deadly nightshade (*Atropa belladonna*) and in the thorn-apple, the fruit of *Datura stramonium*. It is crystalline, melts at 115·5°, and is very poisonous. It exercises a "mydriatic" action—that is, when dropped in dilute solution on the eye, it expands the pupil: for this reason it is employed in ophthalmic surgery. It is optically inactive. On heating with hydrochloric acid or caustic soda at 120°, it takes up water and yields *tropine* and *tropic acid:*

$$\underset{\text{Atropine}}{C_{17}H_{23}O_3N} + H_2O = \underset{\text{Tropine}}{C_8H_{15}ON} + \underset{\text{Tropic acid}}{C_9H_{10}O_3}.$$

It can be regenerated from these two substances by the action of hydrochloric acid. Atropine is, therefore, the tropine ester of tropic acid, which is α-phenyl-β-hydroxypropionic acid,  $C_6H_5{\cdot}CH<^{CH_2OH}_{COOH}$. The constitution of tropine is probably a carbon ring of seven atoms with a "nitrogen-bridge,"



This formula was proposed by Willstätter and is based on the decomposition-products of tropine. They are

1. *Methylsuccinimide*, (I.) indicating the presence of a tetrahydropyrrole-nucleus.*

2. *Tropidine*, obtained through elimination of water by heating with potassium hydroxide or dilute sulphuric acid:

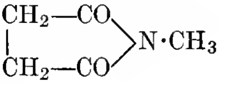
$$\underset{\text{Tropine}}{C_8H_{15}ON} - H_2O = \underset{\text{Tropidine}}{C_8H_{13}N}.$$

Tropidine can be converted into α-ethylpyridine (II.), proving that tropine contains a pyridine-ring.

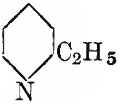
---

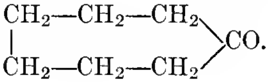
* *Cf.* footnote, **459**.

3. Ecgonine (476) is a carboxylated tropine: it breaks down to suberone (III.), indicating the presence of a ring of seven carbon atoms in the tropine molecule. It has also been established by the usual methods that tropine is a tertiary base, and contains a hydroxyl-group:

I. 

$$\left.\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\right\rangle N\cdot CH_3\ ;$$

II. 

III. 

$$\left.\begin{array}{l}CH_2-CH_2-CH_2\\ |\\ CH_2-CH_2-CH_2\end{array}\right\rangle CO.$$

Cocaïne, $C_{17}H_{21}O_4N$.

476. On account of its use as a local anæsthetic, *cocaïne* is the best known of the alkaloids present in coca-leaves (*Erythroxylon coca*). It is crystalline, is readily soluble in alcohol, and melts at 98° On heating with strong acids, a benzoyl-group and a methyl-group are eliminated, with formation of *ecgonine*, $C_9H_{15}O_3N$, so that the formula of cocaïne may be written

$$C_9H_{13}O_2N(OCH_3)(COC_6H_5).$$

By benzoylating and methylating ecgonine, cocaïne is regenerated. Ecgonine is a carbonyl-derivative of tropine.

Morphine, $C_{17}H_{19}O_3N$.

477. *Morphine* is the longest-known alkaloid: it was obtained from opium in 1806 by SERTÜRNER. Opium is the dried juice of the seed-capsules of *Papaver somniferum*, a variety of poppy. It is a very complicated mixture, containing caoutchouc, fats, resins, gums, sugars, proteïns, mineral salts, meconic acid,

$$(CH_3O)_2C_6H_2(CH_2OH)(COOH),$$

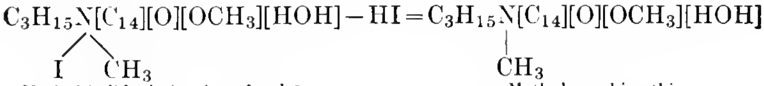
some more organic acids, and other substances, together with numerous alkaloids. Twenty of the last-named have been identified: of these morphine is present in largest proportion, and constitutes about 10 per cent. of opium.

Morphine is crystalline, and melts with decomposition at 230°. It is slightly soluble in water, is without odour, and is employed as an anodyne and narcotic.

478. The reactions of morphine indicate that one of its three oxygen atoms is linked as phenolic hydroxyl, proved by its solubility in alkalis; the second is present as alcoholic hydroxyl; and the third has an ether-linkage. On distillation with zinc-dust it yields phenanthrene, $C_{14}H_{10}$, so that the empirical formula may be expanded to

$$C_{17}H_{19}O_3N = C_3H_{16}N[C_{14}][O][OH][HOH].$$

Treatment with methyl iodide in alkaline solution methylates the phenolic hydroxyl; and the addition of methyl iodide at the nitrogen proves morphine to be a tertiary base. The product formed is identical with the methyl-iodide derivative of codeïne. On treatment of this substance with aqueous sodium hydroxide, hydriodic acid is eliminated, and another tertiary base containing a like number of carbon atoms formed. It is called *methylmorphimethine:*

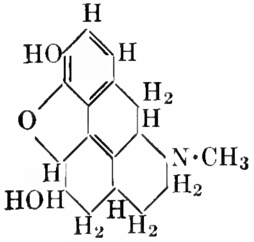


$$\underset{\diagup\ \diagdown \atop I \quad CH_3}{C_3H_{15}N}[C_{14}][O][OCH_3][HOH] - HI = \underset{| \atop CH_3}{C_3H_{15}N}[C_{14}][O][OCH_3][HOH]$$

Methyl-iodide derivative of codeïne   Methylmorphimethine

On heating with acetic anhydride, methylmorphimethine yields a product free from nitrogen and one containing nitrogen. The first is the monomethyl ether of a dihydroxyphenanthrene, convertible by further methylation into a synthetic product, dimethylmorphol (**447**), a reaction indicating its structure. The second is *hydroxyethyldimethylamine*, $CH_2OH{\cdot}CH_2{\cdot}N(CH_3)_2$.

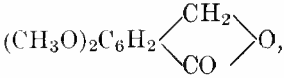
By combining these facts with others it has been possible to assign provisionally to morphine the structural formula



.

It represents morphine as a combination of a partially hydrogenated dihydroxyphenanthrene containing an ether-linked oxygen atom with a hydrogenated pyridine-nucleus having the nitrogen atom linked to methyl.

Narcotine, $C_{22}H_{23}O_7N$.

479. *Narcotine* is present in opium to the extent of about 6 per cent., its percentage being next to that of morphine. It is crystalline, melts at 176°, and is slightly poisonous. It is a weak tertiary base, its salts readily undergoing hydrolytic dissociation. It contains three methoxyl-groups, so that its formula can be written $C_{19}H_{14}O_4N(OCH_3)_3$. *Nornarcotine* has the formula $C_{19}H_{14}O_4N(OH)_3$. On hydrolysis, narcotine yields the anhydride of meconic acid, or *meconin*,  $(CH_3O)_2C_6H_2{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, and *cotarnine*, $C_{12}H_{13}O_3N$, a derivative of *iso*quinoline. Bromine converts narcotine into dibromopyridine.

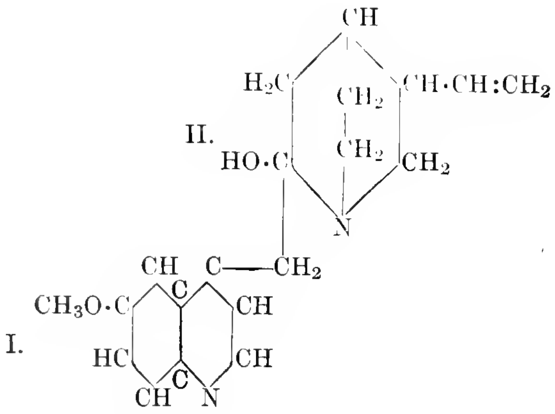
Quinine, $C_{20}H_{24}O_2N_2$.

480. The barks of certain trees of the *Cinchona* and *Remya* families contain a great number of alkaloids: of these twenty-four have been isolated, but it is probable that more are present. The most important of them, on account of its anti-febrile effect, is *quinine*. *Cinchonine*, $C_{19}H_{22}ON_2$, is the next best-known: its physiological action is similar to that of quinine, but is less pronounced.

In addition to alkaloids, these barks contain various acids, such as quinic acid, quinovic acid, and quinotannic acid: neutral substances, such as quinovin, quina-red, etc., are also present.

Quinine is very slightly soluble in water, and is lævo-rotatory. In the anhydrous state it melts at 177°, and at 57° when it contains three molecules of water of crystallization. It is a strong base, and both N-atoms are tertiary. It unites with two equivalents of an acid. In dilute solution the salts of quinine exhibit a splendid blue fluorescence, which serves as a test for the base.

The constitution of quinine has been elucidated, chiefly through the researches of Skraup and of Königs, the latter assigning to it the formula



which expresses the following properties of quinine. On fusion with potassium hydroxide quinine yields quinoline, p-*methylquinoline* or *lepidine*, and p-*methoxyquinoline* from the part of the molecule numbered I. in the structural formula; and β-ethylpyridine from part II. On oxidation, $\alpha\beta\gamma$-pyridinetricarboxylic acid is obtained, also from part I. In addition, quinine is a ditertiary base, and contains a hydroxyl-group and a methoxyl-group. Its additive power indicates the presence of a double carbon bond.

Strychnine, $C_{21}H_{22}O_2N_2$.

481. Three extremely poisonous alkaloids, ***strychnine, brucine,*** and *curarine*, are present in the seeds of ***Strychnos nux vomica,*** as well as in others of the *Strychnos* family. Little is known of the chemical nature of curarine, although it has been much studied from a physiological standpoint: when administered in small doses, it produces total paralysis. Strychnine and brucine cause death, preceded by tetanic spasms—that is, contraction of the muscles; curarine is, therefore, employed as an antidote.

Strychnine is crystalline, and melts at 265°; it is almost insoluble in water. It is a monohydric, tertiary base, only one of its N-atoms exhibiting basic properties. On fusion with caustic potash, it yields quinoline and indole; and when distilled with slaked lime, it is converted into β-picoline (**452**). Heating with zinc-dust produces carbazole (**441**) and other substances.

INDEX.

The basis of the arrangement of this index is two-fold:
(1) The principal references are in old-style figures.
(2) Where a reference is a sub-division of a principal heading, it is indented one *em space* for each word of the principal heading not repeated. Portions of words followed by a hyphen are treated as words for the purposes of this arrangement.

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